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DESIGN AND OPERATION OF A MOLECULAR OSCILLATOR*

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Abstract

Theoretical implications of the design of a two-level maser of the molecular-beam type are presented. The design and operation of a microwave maser that employs a beam of ammonia molecules are described.

I. Introduction

A notable advance in the technique of molecular-beam spectroscopy in recent years has been the development of a device called the "maser" (a device involving a beam of molecules which gives "Microwave Amplification by Stimulated Emission of Radiation") by Gordon, Zeiger and Townes,[1] who employed a molecular beam of ammonia in their first experiment. The gas maser is the precursor of the solid-state masers[2,3] in which paramagnetic crystals are used. These masers are already being put to use in radio astronomy. Because of a fairly good collimation of the beam, the Doppler broadening is small; the emission line is approximately 7 kc. wide. The mean frequency deviation of an oscillating maser is quoted as a few parts in 10^{10}. The gas maser provides a frequency standard of high precision and thus it can be used for operation as an "atomic clock". Aside from its use as a spectrometer, the gas maser has recently been employed to secure a direct experimental verification[4] of one postulate of the Special Theory of Relativity, the constancy of the velocity of light.

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The principles of operation of this device can be extended by using other molecules, for example, alkali halides. There must be some modification in the construction of the beam sources, but the range of frequency standards[5] will thereby be extended. It is also conceivable that the device may provide a means of verifying a prediction of the General Theory of Relativity concerning the influence of the gravitational field on time. Two spectral lines generated by two identical atoms (or molecules) in the same quantum trasition, one atom being situated in very high gravitational potential (for example, close to the sun), and the other in lower gravitational potential (for example, on earth), differ in frequency. The radiation reaching the earth from the distant atom has a longer wavelength than the radiation generated on earth.

The operation of the maser relies on the possibility of obtaining a beam of molecules, virtually all of which are in a quantum state of energy higher than other available states and from which they may be induced to make a transition to a state of lower energy. The balance of the energy appears as radiation. The "state selection" of the molecules has been accomplished in the maser by means of an inhomogeneous electric field that sorts the molecules in the beam, according to their quantum states, as they traverse it. The state-selected beam then enters a tuned microwave cavity in which, under the influence of a radiation field in the cavity, the beam emits power. If a state-selected beam of sufficient strength is sent into the cavity, the radiation emitted by the beam will be of sufficient intensity to compensate for the loss in the cavity wall, and a stationary wave pattern can be set up in the cavity. The cavity is then said to be functioning as an oscillator.

The state selection by the static fields depends on the differential Stark effects on the molecules in the several quantum states. The r-component of the force exerted upon a molecule is given by

$$F_r = -\frac{dW}{dE}\frac{\partial E}{\partial r}, \tag{1}$$

where W is the potential energy of the molecule in the electric field E. The force F_r on the molecule depends, therefore, not only on the field gradient but also on the quantum state of the molecule (which determines W for a given electric field). Hence, the separation of molecules is brought about in the inhomogeneous field. A molecular beam of ammonia having isolated pairs of rotation-inversion states (each pair of levels is described by the rotational quantum numbers J and K, with the inversion index sup-

pressed) is ideal in this respect, since the forces associated with the two states are opposite in sign for limited values of the field. Thus

$$F_r = \mp \frac{\frac{\tilde{\mu}^2 M^2 K^2}{J^2(J+1)^2}}{\left[\left(\frac{h\nu_0}{2}\right)^2 + E^2\tilde{\mu}^2 \frac{M^2K^2}{J^2(J+1)^2}\right]^{\frac{1}{2}}} E \frac{\partial E}{\partial r}, \tag{2}$$

where $\tilde{\mu}$ is the electric dipole moment of the molecule; ν_0, the inversion frequency; J, the quantum number for the total angular momentum; and K, M, the quantum numbers obtained from the projection of J along the molecular axis, and along a space-fixed axis. If the field structure has axial symmetry, and the field increases with lateral displacement from the axis up to a value $E_{max.}$, then the molecules in the inversion state of higher energy emerging from a source that has small angular divergence about the axis of the field are subject to a lateral force inwards and can be trapped into a microwave cavity (Fig. 1), provided that their transverse velocity does not exceed a critical value v_c given by

$$W_c = \tfrac{1}{2} m v_c^2,$$

where W_c is the Stark energy at the surface of the focuser. The emitted power and the (angular) frequency of oscillation ω_1 of the stationary waves

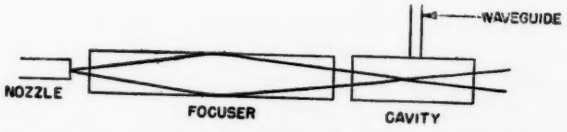

FIG. 1. Diagram showing the essential parts of the maser oscillator.

in the cavity, slightly modified by the lack of perfect tuning of the cavity to the resonant (angular) frequency ω_0 of a particular inversion transition, are given[6,7] by

$$P_B = \tfrac{1}{2} G^2 (N'\hbar\omega_1) \left(\frac{L}{l}\right)^2 \left(1 + \log \frac{l}{2L}\right) \left(\frac{R}{v_c}\right)^2 \frac{\sin^2\theta}{\theta^2} \tag{3}$$

$$\frac{\omega_1 - \omega_0}{\omega_0} = \frac{\omega_c - \omega_1}{\omega_c} \frac{2Q}{\omega_0} \frac{1}{\tau_1}, \tag{4}$$

where

$$\theta = \frac{1}{\sqrt{2}} \frac{l}{L} \frac{R}{v_c} \left(1 + \log \frac{l}{2L}\right)^{\frac{1}{2}} [(\omega_1 - \omega_0)^2 + G^2]^{\frac{1}{2}}; \tag{5}$$

τ_1 is very nearly equal to R/v_c (*see* Appendix); N′ represents the flux of molecules in the cavity; G, the electric field amplitude in the cavity; l, L, the lengths of the focuser and cavity, respectively; R, the cross-section radius of the focuser and cavity; ω_c, the resonant frequency of the cavity; and Q, the quality factor of the cavity. The oscillation condition is given by

$$\frac{1}{Q} \leqslant \frac{4\sqrt{\pi}}{\hbar} \frac{N\bar{\mu}^2}{a^3} v_c^2 L \left(1 + \log \frac{l}{2L}\right), \tag{6}$$

where N represents the excess of molecules in the inversion state of higher energy in the incident beam; and a, the most probable velocity of the molecules in the beam source.

II. General Experimental Design

To find the operating characteristics of the maser explicitly, we write[8] the critical velocity occurring in the oscillation condition as follows:

$$W_c = \tfrac{1}{2} m v_c^2 = \tfrac{1}{2}\left[(h\nu_0)^2 + 4E^2_{max.}\mu^2 \frac{M^2K^2}{J^2(J+1)^2}\right]^{\frac{1}{2}} - \tfrac{1}{2} h\nu_0. \tag{7}$$

The oscillation condition can then be written

$$E_{max.} \geqslant \frac{J(J+1)}{MK} \frac{(h\nu_0)^{\frac{1}{2}}}{\bar{\mu}^2 m^{\frac{1}{2}}} \frac{1}{(QA)^{\frac{1}{2}}} \frac{T^{\frac{3}{2}}}{N^{\frac{1}{2}}} \left\{1 + \frac{1}{2h\nu_0\bar{\mu}^2\sqrt{m}} \frac{1}{QA} \frac{T^{3/2}}{N} + \ldots\right\} \tag{8}$$

where

$$A = \frac{(32\pi^3)^{\frac{1}{2}}}{hk^{3/2}} L \left(1 + \log \frac{l}{2L}\right). \tag{9}$$

The terms in the braces in (8) decrease rather rapidly for $N \geqslant 10^{10}$.

Rather than the maximum field of the focuser, the potential given to the rods of the focuser is actually measured. The relation between the focusing voltage V and the field E is determined by the geometry of the focuser. In the actual experimental arrangement a $2p$-pole focuser[9] was used. This consists of $2p$-parallel rods of metal arranged symmetrically on a cylindrical surface. The field arising from the geometry of the focuser has a cross-section component given by

$$E(r, \phi) = \frac{C_p V \left(\frac{r}{b}\right)^{\frac{1}{2}p-1}}{\left[1 + \left(\frac{r}{b}\right)^{2p} - 2\left(\frac{r}{b}\right)\cos p\phi\right]^{\frac{1}{2}}}, \tag{10}$$

where r is the radial displacement, and ϕ is the azimuthal angle.

Furthermore,

$$C_p = \frac{p}{4b\left(\frac{\xi_0 - \rho_0}{b}\right)^{\frac{1}{2}p} S_p}\ ;\ S_p = \frac{\sum_{n=0}^{\infty}\left(1 - \frac{\rho_0}{\xi_0}\right)^{\frac{1}{2}np}}{(2n+1)}\ ;$$

$$b = \pm\left[\xi_0(\xi_0 - \rho_0)\right]^{\frac{1}{2}},$$

where ρ_0 is the cross-section radius of the rods, ξ_0 that of the focuser and $\rho_0 \ll \xi_0$. The relation between the maximum field and the voltage is given approximately by

$$E_{max.} \approx \frac{p}{2\xi_0} V, \tag{11}$$

with the condition $\rho_0 \ll \xi_0$ that was assumed in the derivation of (10). Combining (11) with (8), we can write the following relation for the minimal oscillation condition, which is valid within a limited range of N:

$$V_0 \approx \frac{2\xi_0}{p} \cdot \frac{J(J+1)}{MK} \cdot \frac{(h\nu_0)^{\frac{1}{2}}}{\bar{\mu}^2 m^{\frac{1}{2}}} \frac{1}{(QA)^{\frac{1}{2}}} \frac{T^{\frac{3}{4}}}{N^{\frac{1}{4}}}$$

$$\times\left(1 + \frac{1}{2h\nu_0\bar{\mu}^2\sqrt{m}} \cdot \frac{1}{QA} \cdot \frac{T^{3/2}}{N} + \cdots\right), \tag{12}$$

where V_0 is the starting voltage for producing self-sustained oscillations in the cavity for a given density N (in the beam source) of the molecules in the inversion state of higher energy. The oscillation condition depends, therefore, on the cross-section radius of the focuser, the lengths of the cavity and focuser, the properties of the molecule (m, $\bar{\mu}$, ν_0), the quantum state of the molecule (J, K, M) and the thermal conditions of the source (N, T). The estimated values of V_0 for two values of the density are:

$$N = 10^{10};\ \ 10^{11}$$

$$V_0 = 9 \text{ kv.};\ \ 2{\cdot}15 \text{ kv.}$$

We shall now describe the cavity. There are two properties of the cavity to be considered: the quality factor Q, and the mode of the electromagnetic oscillation in the cavity. If cavity tuning is to be accomplished by varying its diameter alone, then the TM_{010} mode is the appropriate one. This mode is also associated with a high figure of merit. The frequency of the mode is determined as $\nu = 2{\cdot}405\, c/\pi D$, where D is the diameter of the cavity, and c is the velocity of light. The transverse and longitudinal components of the field in a circular wave-guide are indicated in Fig. 2 (*a*).

Figure 2 (*b*) illustrates the coupling of the cavity to an external wave-guide system through an iris located halfway between the ends of the cavity. The external Q_E, which measures the loss of power through the iris, and the internal

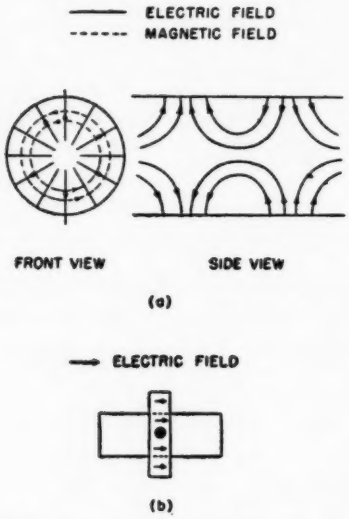

FIG. 2. (*a*) Field configuration in a circular wave-guide. (*b*) Coupling of wave-guide section to cavity.

Q_0, which measures the dissipative loss in the wall of the cavity, are both experimentally determined (with low precision) as

$$Q_0 = \frac{2}{1+r}\frac{\nu}{\Delta\nu}\,; \quad Q_E = \frac{2}{1-r}\frac{\nu}{\Delta\nu}\,; \quad \frac{1}{Q} = \frac{1}{Q_0} + \frac{1}{Q_E},$$

where ν is the centre frequency; $\Delta\nu$, the width of the cavity mode resonance; and r, the reflection coefficient. It is desirable to have the external Q_E large compared with Q_0, in order to produce oscillations in the cavity most easily.

III. DETECTION SYSTEM

The method of detection depends on the amount of output power. This can be estimated,[6] under saturation conditions, from the formula

$$P_{out.} = \frac{\omega_1 W}{Q_E},$$

where W is the energy stored in the cavity. With the typical values A = 1 cm.², l = 20 cm., L = 10 cm., $v_c = 10^3$ cm./sec., Q_E = 100,000, we obtain

$$P_{out.} \approx 3 \times 10^{-10} \text{ watt.}$$

The noise power that is in competition with the signal power from the cavity is kTb, or 10^{-13} watt, with b equal to a few megacycles. The observation of the signal is feasible if we employ a superheterodyne method of detection. A block diagram of the microwave circuit used in the actual experiment is shown in Fig. 3. The power from the signal generator, tuned to the 3-3

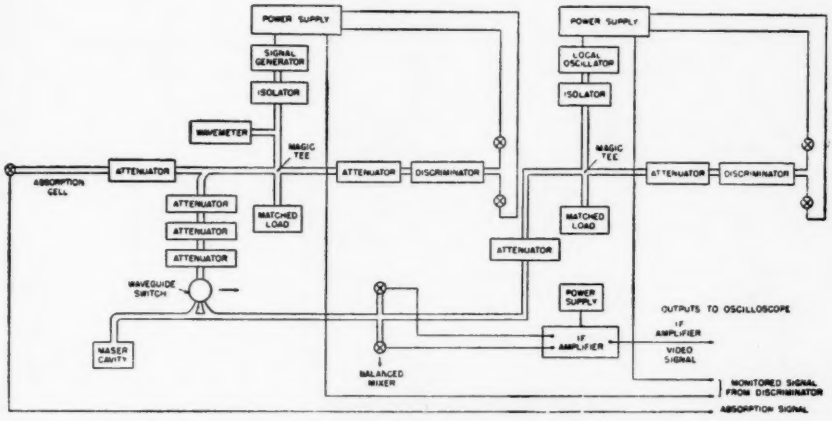

FIG. 3. Block diagram of the microwave circuit.

inversion frequency, is transmitted to the absorption cell containing ammonia gas at very low pressure (50 microns) and to the discriminator, by using a magic Tee. A directional coupler is used to transmit part of the power to the maser cavity through the attenuators. The power reflected from the cavity is transmitted to a balanced mixer. The output from the local oscillator (a second klystron tuned 30 mc. away from the frequency of the signal generator) is transmitted to the balanced mixer, and also to the discriminator. These two signals are mixed in the rectifying crystals of the balanced mixer and a signal with the 30 mc. frequency difference is amplified by the intermediate-frequency amplifier (IF strip). The output of the IF strip is exhibited on the oscilloscope. The signal generator is modulated and the local oscillator stabilised. The discriminator in the circuit is designed[10] for the purpose of stabilising the local oscillator or the signal generator.

IV. DESIGN OF AN AMMONIA MASER

Figure 4 illustrates an ammonia manifold that is the source of the molecular beam. Figure 5 shows the parts of the maser assembly in the vacuum

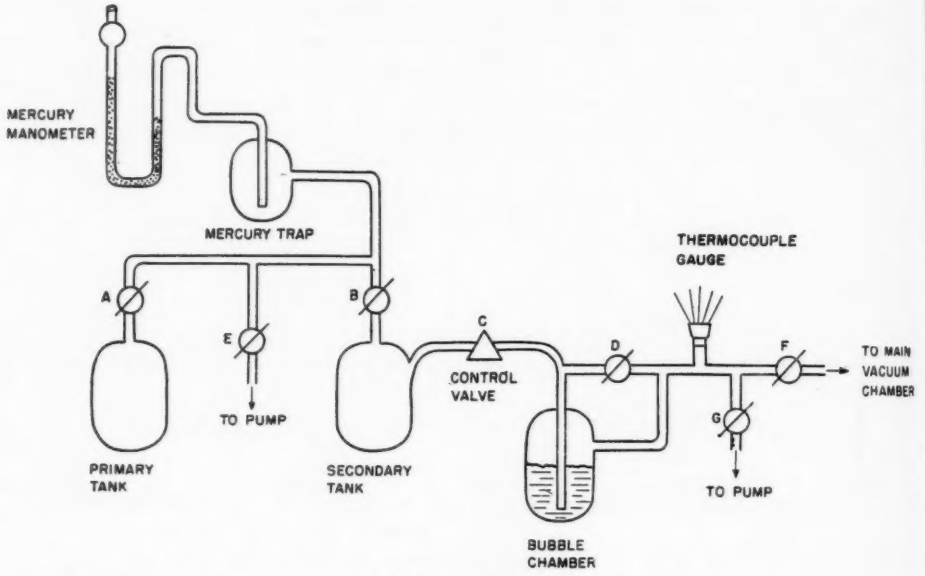

FIG. 4. Gas manifold.

chamber. The manifold consists essentially of an ammonia tank, a needle valve, and a bubble chamber. The system is evacuated to a pressure of 10^{-3} mm. by using two forepumps. The stop-cocks E, G are provided to isolate the manifold from the pumps in operating condition. The primary tank contains ammonia at very high pressures (several atmospheres). This pressure is scaled down to one atmosphere in the secondary tank. The ammonia gas bubbles through the Octoil in the chamber when the stop-cock D is closed and the needle valve C is slightly opened. Octoil "S" is used in the bubble chamber because it has a low vapour pressure of 10^{-6} mm. at room temperature.

The main vacuum chamber, 30 in. long, and 5 in. in diameter, is made of stainless steel. It is closed on top with a lid that supports the main parts of the maser assembly, which are held in position by steel mounts with Teflon spacers. To prevent the vapours of the oil in the diffusion pump at the lower end of the chamber from condensing on the parts, a baffle is

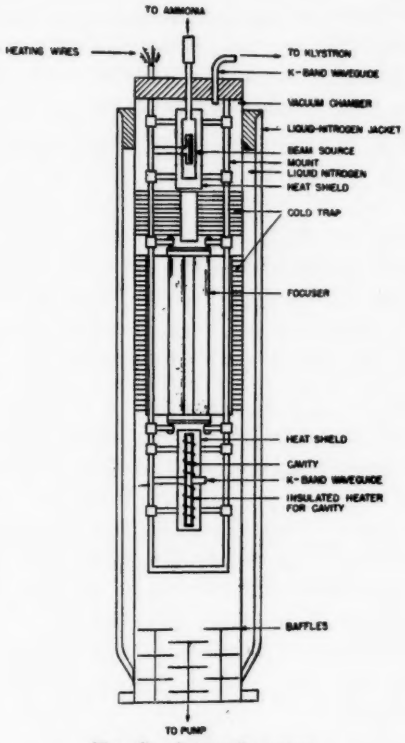

FIG. 5. Ammonia maser.

provided. The whole chamber is provided with a liquid-air jacket that is welded to it. The jacket is an evacuated double wall; it is used to cool the internal parts of the chamber, especially the fin-like condensers in thermal contact with the inside wall.

The gas from the manifold enters the beam source in the chamber. The beam source is a cylinder of stainless steel, 3 in. long and 0·5 in. in diameter. It has a nozzle that is constructed as follows: a long ribbon of nickel, 0·015 in. wide, is fed between interlocking geared wheels so that the ribbon is transversely corrugated. The corrugations are parallel grooves of semicircular cross-section shape, with a diameter of approximately 5 mils. When alternately corrugated and uncorrugated strips are stacked, narrow channels are formed between the layers in a rectangular array that has a honeycomb structure to serve as a nozzle. Since the beam source is likely

to cool to a very low temperature when the vacuum chamber is cooled to liquid-nitrogen temperature, provision must be made for its heating in order to prevent condensation of ammonia. The beam source is an independent unit that can easily be taken out of the chamber and replaced by another of suitable design for work with other molecules.

The focuser consists of 8 rods of stainless steel, approximately 0·062 in. in diameter. The rods are spaced equally on a cylindrical surface and supported by Teflon spacers. The cross-section radius of the multipole focuser is 0·2 in. and its length is 10 in. The rods are sufficiently far apart to support a potential difference of 30 kv., or so, without sparking. The two sets of alternate rods are connected to thick copper wires that are taken out of the vacuum chamber through glass insulation inside the supporting steel tubes on which the maser parts are mounted.

The cavity is designed for the TM_{010} mode. It is a cylindrical cavity, open at both ends, made of coin silver. The cross-section diameter is very close to 0·378 in. at room temperature, and it is 4·74 in. long. The diameters of the cavity and iris are brought to the desired dimensions by observing resonant frequency and external Q, and correcting them by lapping the cavity. The wave-guide connecting the cavity to the external system through the iris has its shorter side parallel to the axis of the cavity. It is closed by a mica window so as to be vacuum-tight. Exact tuning of the cavity can be accomplished under actual operating conditions by electrical heating. For this purpose, the cavity is enclosed firmly in a lavite block, on which a bifilar heater of nichrome wire is wound. Bifilar winding is essential to exclude from the cavity the magnetic field that will affect the resonant frequency of the molecule. The focuser is surrounded by the structure shown in Fig. 6. This consists of a set of copper discs, each having a circular opening, approximately 2 in. in diameter, through which the focuser passes. The purpose of introducing the baffles is to provide a large cold surface on which extraneous molecules, especially the inactive ones scattered by the focuser, can be trapped.

The alignment of the beam source, the focuser, and the cavity is optically tested to ensure that the molecules emerging from the beam source actually pass through the focuser and the cavity.

V. MASER OPERATION

During experimentation we should aim at achieving a pressure of 10^{-6} mm. in the vacuum chamber when the molecular beam is on. The gas manifold is also evacuated to a pressure of 10^{-6} mm. The stop-cock F is

open to the main chamber, and G, E closed. Then the control valve is closed, and the gas from the primary tank admitted into the secondary tank at a pressure of approximately one atmosphere, as indicated by the manometer. The ammonia gas can be made free of any possible contamination as follows. The stop-cock B is closed, and the secondary tank cooled to liquid-nitrogen temperature. The gas crystallises in the tank. Now, C may be opened. The presence of residual gases in the tank is indicated by a slight rise in the pressure, as indicated by the ion-gauge meter. These gases are pumped out, and thereby the ammonia gas is purified. The valve C is closed again, and the crystallised ammonia exposed to room temperature. When the stop-cock D is closed and the control valve slightly opened, the gas bubbles through the Octoil at a uniform rate. The flow rate determines the number of molecules per second that effuses into the vacuum chamber. With tubing of 0·25 in. diameter in the bubble chamber, one bubble per second is the optimum rate; this rate can be varied conveniently during operation. Before the gas is allowed to enter the vacuum chamber, the chamber is cooled to liquid-nitrogen temperature, and then the cavity is heated so that it resonates with the 3–3 inversion line of ammonia.

Cavity tuning is accomplished as follows. The power from the signal generator, transmitted through the absorption cell, is monitored. The wavemeter is set to the frequency of the 3–3 line (23,870 mc.), which is correct within a few megacycles. (This approximate setting is made to ensure that we are in the proper region.) When the klystron is tuned to this frequency, the klystron mode shows the pip of the wavemeter as it is observed on the oscilloscope. When ammonia is introduced into the cell at a pressure of approximately 50 microns a sharp absorption line appears. The wavemeter is set to the absorption line, as well as it can be, visually. At this stage, the *y*-input to the oscilloscope is taken from one of the crystals of the balanced mixer so that the signal is the klystron mode (reflected from the maser cavity) with the wavemeter pip. For this observation it is necessary to use a 20-db. transistor amplifier. The resonant frequency of the cavity is made to coincide with the wavemeter setting by carefully adjusting the heating current; thereafter the wavemeter is detuned. It will be necessary to tune the cavity slightly around this setting when an actual search for the emission line is being carried out.

Now the IF strip is brought into the circuit. The output of the local oscillator at a frequency of 30 mc. away from inversion frequency is transmitted to the balanced mixer. The output of the IF amplifier now becomes the *y*-input of the oscilloscope. The local oscillator is stabilised at a frequency $\nu_0 \pm 30$ mc., as follows. The output of the discriminator crystals

is monitored. The discriminator cavity is tuned until the cavity-mode signal appears on the oscilloscope. The symmetrical discriminator pattern is obtained by balancing the outputs of the two discriminator crystals. The sweep is then removed and the local oscillator stabilised.

The cavity is now set in the narrow region about the inversion frequency ν_0, the local oscillator is stabilised, and the signal generator is swept about the inversion frequency. The output of the IF amplifier is seen on the oscilloscope as a spike. By slightly tuning the discriminator cavity in the local-oscillator circuit, the spike is observed to pass through a minimum that indicates the setting of the maser cavity. The power transmitted from the signal generator to the maser cavity is attenuated approximately 80 db. The control valve is then opened slightly and the gas allowed to bubble through the Octoil at a rate of one bubble per second. Voltages of from $\pm$ 5 kv. to $\pm$ 15 kv. are applied to the focuser rods. The sweep on the signal generator is gradually cut down while the signal is kept in view. Finally, the signal generator is stabilised, and the local oscillator swept to exhibit the maser oscillation signal on the oscilloscope.

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REFERENCES

1. Gordon, J. P., Zeiger, H. J. and Townes, C. H. — *Phys. Rev.*, 1955, **99**, 1264.
2. Scovil, H. E. D., Feher, G. and Seidel, H. — *Ibid.*, 1957, **105**, 762.
3. Strandberg, M. W. P. Davis, C. F. Jr., Faughnan, B. W., Kyhl, R. L. and Wolga, G. J. — *Ibid.*, 1958, **109**, 1988.
4. Cedarholm, J. P., Bland, G. F., Havens, B. L. and Townes, C. H. — *Ibid.*, Letters, 1958, **1**, 342.
5. Peter, M. and Strandberg, M. W. P. — "Theoretical and experimental study of molecular-beam microwave spectroscopy," *Technical Report* 336, Research Laboratory of Electronics, M.I.T., August 26, 1957.

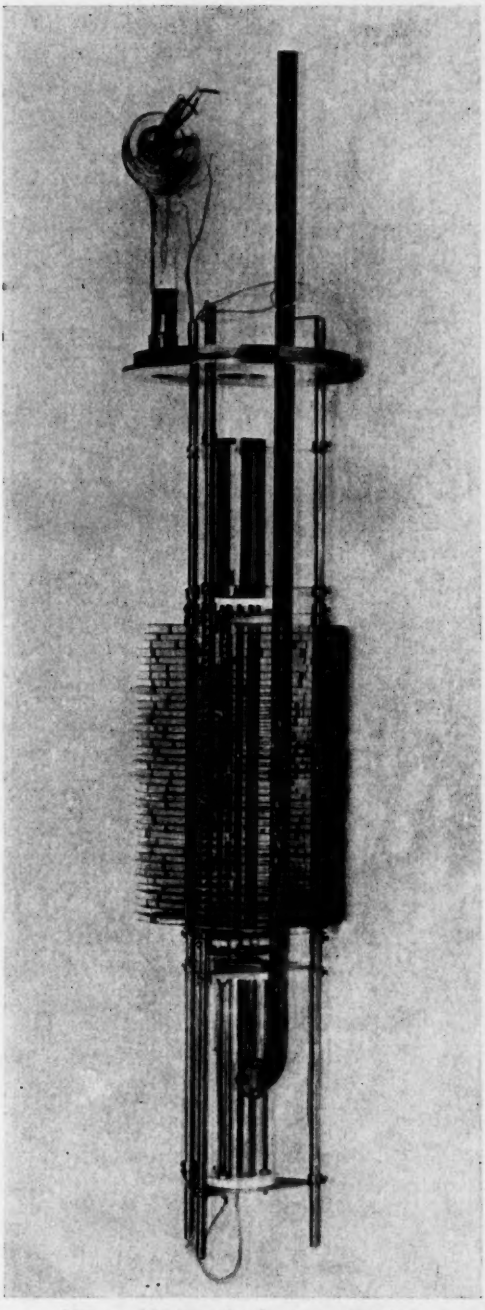

FIG. 6. Photograph of maser assembly.

6. Venkates, H. G. and Strandberg, M. W. P. "Operating characteristics of a molecular-beam maser" (to be published in *J. Appl. Phys., U.S.A.*).

7. Shimoda, K. .. *J. Phys. Soc. Japan*, 1957, **12**, 1006.

8. Townes, C. H. and Schawlow, A. L. *Microwave Spectroscopy*, McGraw-Hill Book Company, Inc., New York, 1955.

9. Vonbun, F. O. .. "A multipole separator for masers," *Engineering Report, NRE*-1203, U.S. Army Signal Engineering Laboratories, Fort Monmouth, N.J., April 1957.

10. Wolga, G. J. .. "Microwave resonance studies of absorption and hyperfine interactions of F centers in alkali halide crystals," *Ph.D. Thesis*, Department of Physics, M.I.T., August 1957.

APPENDIX

The time τ_1, introduced in Eq. (4), for the frequency pulling is given[6] by

$$\tau_1 = \frac{1}{3}\frac{L}{a}\frac{\int_{y=0}^{a}\int_{x=y}^{b}\frac{y}{x^2}e^{-x^2}\,dx\,dy + \int_{y=0}^{a}\int_{x=0}^{y}\frac{x}{y^2}e^{-x^2}\,dx\,dy}{\int_{y=0}^{a}\int_{x=y}^{b}\frac{y}{x}e^{-x^2}\,dx\,dy + \int_{y=0}^{a}\int_{x=0}^{y}\frac{x}{y}e^{-x^2}\,dx\,dy},$$

where

$$a = \frac{L}{R}\frac{v_c}{a}\,; \quad b = \frac{l}{2R}\frac{v_c}{a}.$$

The integral sum in the numerator is evaluated as

$$a\left(1-\frac{a}{2b}\right) + \sum_{n=1}^{\infty}\frac{(-1)^n}{(2n-1)\,n!}\left\{\frac{1}{2}a^2b^{2n-1} - \frac{a^{2n+1}}{2n+1} - \frac{1}{2}a^{2n-1}\right\}$$

$$= a\left(1-\frac{a}{2b}\right) - \left(\frac{1}{2}ba^2 - \frac{1}{3}a^3 - \frac{1}{2}a\right)$$

$$+ \frac{1}{6}\left(\frac{1}{2}a^2b^3 - \frac{1}{5}a^5 - \frac{1}{2}a^3\right) + \ldots.$$

Since, in practice, $a \ll 1$ and $b \ll 1$, we may neglect the third and higher powers and write for the integral sum in the numerator

$$\frac{3}{2}a\left(1-\frac{a}{3b}\right) = \frac{3}{2}\frac{L}{R}\frac{v_c}{a}\left(1-\frac{2L}{3l}\right).$$

The integral sum in the denominator has already been evaluated.[6] It is equal to

$$\frac{1}{2}\frac{L^2}{R^2}\left(\frac{v_c}{a}\right)^2\left(1+\log\frac{l}{2L}\right).$$

The time τ_1 is then given by the expression

$$\tau_1 = \frac{R}{v_c}\frac{1-\frac{2}{3}\frac{L}{l}}{1+\log\frac{l}{2L}}.$$

In the experimental design $l \approx 2L$, and hence we may write

$$\tau_1 \approx \frac{2}{3}\frac{R}{v_c}.$$

ON THE APPLICATION OF THE MATRIX CALCULUS IN THE THEORY OF GEOMETRICAL DIFFERENCE EQUATIONS

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Introduction

1. *Notations.*—The purpose of the present paper is to show that some results in the theory of geometrical difference equations can be proved by the use of the matrix calculus. In particular, the so-called regular case may be treated completely whereas the irregular case brings some difficulties which cannot be overcome. It may be mentioned that the analytical behaviour of the solutions of a geometric difference equation has been treated completely by Trjitzinsky in a very extensive paper.[1]

Let q be a real parameter, $0 < q < 1$. The operator of the geometrical difference is defined by

$$\theta f(x) = \frac{f(qx) - f(x)}{x(q-1)}; \quad \theta^{r+1} f = \theta(\theta^r f)\,(r = 1, 2, \ldots). \tag{1.1}$$

The inverse operator may be expressed by means of an infinite series. If $\theta F(x) = f(x)$, we get[2]

$$F(x) - F(0) = (1-q)\,x \sum_{j=0}^{\infty} q^j f(xq^j). \tag{1.2}$$

The right-hand side is sometimes written as

$$\int_0^x f(x)\,d(q, x). \tag{1.3}$$

The general linear geometrical difference equation may be given in the form

$$\theta y = A(x)\,y + z, \tag{1.4}$$

$y(x)$ being a column vector, z being a given vector and $A(x)$ a given matrix.

[1] *Cf.* (1). [2] *Cf.* (2).

The equation

$$a_0(x)\,\theta^n f + a_1(x)\,\theta^{n-1} f + \ldots + a_{n-1}(x)\,\theta f + a_n(x) f = g(x) \tag{1.5}$$

may be regarded as a special case of (1.4), if we introduce the vector y with the components

$$y_1 = f, \quad y_2 = \theta f, \ldots, \quad y_n = \theta^{n-1} f$$

the vector z with the components

$$z_1 = z_2 = \ldots = z_{n-1} = 0, \quad z_n = g$$

and the matrix

$$\mathrm{A} = \begin{pmatrix} 0 & 1 & 0 & \ldots & 0 \\ 0 & 0 & 1 & \ldots & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & 0 & \ldots & 1 \\ -\frac{a_n}{a_0} & -\frac{a_{n-1}}{a_0} & -\frac{a_{n-2}}{a_0} & \ldots & -\frac{a_1}{a_0} \end{pmatrix}$$

Because of (1.1), the equation (1.2) may be brought into the form

$$y(qx) = \mathrm{B}(x)\, y(x) + \tilde{z} \tag{1.6}$$

where

$$\mathrm{B} = \mathrm{I} - x(1-q)\,\mathrm{A}, \quad \tilde{z} = -x(1-q)\,z \quad (\mathrm{I} \text{ the unit matrix}).$$

Let the function $e_q(t)$ be defined[3] by

$$e_q(t) = \frac{1}{\prod_{r=0}^{\infty} (1 - q^r t)}. \tag{1.7}$$

This meromorphic function may be represented by the power series

$$1 + \frac{t}{1-q} + \frac{t^2}{(1-q)_2} + \ldots + \frac{t^n}{(1-q)_n} + \ldots \tag{1.8}$$

where

$$(1-q)_n = (1-q)(1-q^2)\ldots(1-q^n). \tag{1.9}$$

The series (1.8) is convergent for $|t| < 1$.

[3] *Cf.* (2).

Let $P(t)$ be a matrix, bounded for $|t| \leq t_0$. Then the matrix

$$F[P(t), t] = [I - tP(t)]^{-1}[I - qtP(qt)]^{-1}[F - q^2tP(q^2t)]^{-1} \quad \ldots (1.10)$$

has a meaning for sufficiently small $|t|$. This may be proved as follows: Surely, a certain $|t_1| < t_0$ will exist so that for $|t| < t_1$ each factor

$$I - q^r tP(q^r t) \qquad (r = 0, 1, \ldots)$$

is not singular and that its inverse may be written as

$$I + q^r tQ(q^r t),$$

$Q(t)$ being bounded too. Let m be a bound of the elements of Q and let M be the matrix with all its elements equal to m. Then each element of the matrix (1.10) will be majorized by the elements of the matrix

$$(I + tM)(I + qtM)(I + q^2tM) \ldots \qquad (1.11)$$

Now, this matrix may be developed into the everywhere convergent power series[4]

$$1 + \frac{tM}{1-q} + q\frac{t^2M^2}{(1-q)_2} + \ldots + q^{r(r-1)/2}\frac{t^rM^r}{(1-q)_r} + \ldots \qquad (1.12)$$

and, therefore, each element of (1.10) has a convergent majorant. That means the existence of (1.10) has been proved. If P is a constant matrix all the factors of $F(P, t)$ commute inter each other. Then it is possible to develop $F(P, t)$ into the series

$$1 + \frac{tP}{1-q} + \frac{t^2P^2}{(1-q)_2} + \ldots \qquad (1.13)$$

which is convergent for sufficiently small $|t|$ and with regard to (1.8) may be denoted symbolically by $e_q(tP)$.

2. *The Regular Case.*—We regard the homogeneous equation (1.4), *i.e.*,

$$\theta y = A(x)\, y \qquad (2.1)$$

and assume that $y(0) \neq 0$ exists. Then, $A(x)$ must be bounded for $x = 0$, otherwise the equation [*cf.* (1.6)]

$$y(qx) = [I - x(1-q)A(x)]\, y(x) \qquad (2.2)$$

had no meaning for $x = 0$. Now, one can see immediately that the vector

$$y = F[A(x), x(1-q)]\, y(0) \qquad (2.3)$$

is a solution of (2.2) and also of (2.1). Consequently, the general solution of (2.1) is[5]

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[4] *Cf.* (2). [5] *Cf.* (1).

$$F[A(x),\ x(1-q)]\,R(x)\,y(0), \tag{2.4}$$

where $R(x)$ is q-periodical,

$$R(qx) = R(x).$$

The solution (2.3) is regular in a certain neighbourhood of $x = 0$.

There exists one more way to find the solution of (2.1). We consider the matrix

$$\begin{aligned} S = I &+ (1-q)\,x \sum_{j=0}^{\infty} q^j A(q^j x) + (1-q)^2 x^2 \sum_{j=0}^{\infty} q^{2j} A(xq^j) \\ &\times \sum_{k=0}^{\infty} q^k A(xq^{j+k}) + (1-q)^3 x^3 \sum_{j=0}^{\infty} q^{3j} A(xq^j) \\ &\times \sum_{k=0}^{\infty} q^{2k} A(xq^{j+k}) \sum_{l=0}^{\infty} q^l A(xq^{j+k+l}) + \ldots \end{aligned} \tag{2.5}$$

If A is bounded, the convergence of this series can be proved in the same way as we proved the convergence of (1.10). Replacing A by a matrix M with all its elements equal to m in (2.5), we get

$$\begin{aligned} I + (1-q)\,xM \Sigma q^j &+ (1-q)^2 x^2 M^2 \Sigma q^{2j} \Sigma q^k \\ &+ (1-q)^3 x^3 M^3 \Sigma q^{3j} \Sigma q^{2k} \Sigma q^l + \ldots \\ &= e_q[x(1-q)M] \end{aligned}$$

which is therefore a majorant for (2.5).

Now, we can see immediately that

$$\theta S = A(x)\,S \tag{2.6}$$

and consequently

$$\bar{y}(x) = Sy(0) \tag{2.7}$$

must be a solution of (2.1). Because $S(0) = I$, the solutions (2.7) and (2.3) must be the same, and we see in the same time that

$$S = F[A(x),\ x(1-q)]. \tag{2.8}$$

This formula may be interpreted as an expansion of the infinite matrix product (1.10) which is analogous to the well-known Ω-matrix arising from $A(x)$ by repeated integration.

3. *The Inhomogeneous Equation.*—To find the general solution of the equation

$$\theta y = A(x)\,y + z \tag{3.1}$$

we need a particular solution y^+ and then we get the general solution adding this y^+ to the general solution (2.4) of (2.1). To get the particular solution, we apply the method of the variation of parameters. We set

$$y^+ = \mathrm{F}[\mathrm{A}(x),\ x(1-q)]\, w(x) \tag{3.2}$$

where $w(x)$ is another unknown vector. Then we get

$$\theta y^+ = \mathrm{A}(x)\,\mathrm{F}[\mathrm{A}(x),\ x(1-q)]\, w(x) + \mathrm{F}[\mathrm{A}(qx),\ xq(1-q)]\,\theta w. \tag{3.3}$$

Substituting (3.2) and (3.3) into (3.1) we get

$$z = \mathrm{F}[\mathrm{A}(qx),\ qx(q-1)]\,\theta w \tag{3.4}$$

and we can find w by means of the formula (1.2) or (1.3) as

$$w = \mathring{\sum_{0}} \mathrm{F}[\mathrm{A}(qx),\ qx(1-q)]^{-1}\, z(x)\, d(q,\ x) \tag{3.5}$$

Therefore, the general solution of (3.1) has the form

$$y = \mathrm{F}[\mathrm{A}(x),\ x(1-q)] \times\left[\mathrm{R}(x)\, y(0) + \mathring{\sum_{0}} \mathrm{F}\{\mathrm{A}(qx),\ qx(1-q)\}^{-1}\, z(x)\, d(qx)\right] \tag{3.6}$$

4. *Constant Matrices.*—If the matrix A in (2.1) is a constant one we can represent the solution by means of the function $e_q(t)$ in the same way as the solution of a differential equation may be composed out of exponential functions.

Let P be a non-singular constant matrix which transforms the matrix A into its canonical form J,

$$\mathrm{P}^{-1}\mathrm{AP} = \mathrm{J}. \tag{4.1}$$

Let

$$y = \mathrm{P}u \tag{4.2}$$

then we have

$$\theta u = \mathrm{J}u. \tag{4.3}$$

Applying (2.3) and considering (1.13) we find

$$u(x) = e_q[x(1-q)\,\mathrm{J}]\, u(0) \tag{4.4}$$

and therefore

$$y(x) = \mathrm{P} e_q[x(1-q)\mathrm{J}]\,\mathrm{P}^{-1} y(0). \tag{4.5}$$

Now, J being a canonical matrix, $e_q(t\mathrm{J})$ can be calculated very easily. Let T be one of the "boxes" of J of the order k, belonging to the eigenvalue a of A,

$$\mathrm{T} = \begin{pmatrix} a & 1 & 0 & \dots & 0 & 0 \\ 0 & a & 1 & \dots & 0 & 0 \\ \cdot & \cdot & \cdot & \dots & \cdot & \cdot \\ 0 & 0 & 0 & \dots & a & 1 \\ 0 & 0 & 0 & \dots & 0 & a \end{pmatrix} \tag{4.6}$$

Then we have

$$e_q(t\mathrm{T}) = \sum_{r=0}^{\infty} \frac{t^r \mathrm{T}^r}{(1-q)_r}. \tag{4.7}$$

Calculating the powers of T we find for $r = 0, 1, \dots$

$$\mathrm{T}^r = \begin{pmatrix} a^r & \binom{r}{1} a^{r-1} & \binom{r}{2} a^{r-2} & \dots & \binom{r}{k-1} a^{r-k+1} \\ 0 & a^r & \binom{r}{1} a^{r-1} & \dots & \binom{r}{k-2} a^{r-k+2} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \dots & a^r \end{pmatrix} \tag{4.8}$$

Substituting (4.8) into (4.7) we see that all elements in the main diagonal of (4.7) are

$$\sum_{r=0}^{\infty} \frac{t^r a^r}{(1-q)_r} = e_q(ta).$$

The elements in the first oblique row parallel to the main diagonal are

$$\sum_{r=0}^{\infty} \frac{r t^r a^{r-1}}{(1-q)_r} = t e_q'(ta), \text{ etc.}$$

Therefore

$$e_q(t\mathrm{T}) = \begin{pmatrix} e_q(at) & t e_q'(at) & \dots & \binom{r}{k-1} t^{k-1} e_q^{(k-1)}(at) \\ 0 & e_q(at) & \dots & \binom{r}{k-2} t^{k-2} e_q^{(k-2)}(at) \\ \cdot & \cdot & \dots & \cdot \\ 0 & 0 & \dots & e_q(at) \end{pmatrix}.$$

Now, $e_q(t\mathrm{T})$ is a "box" of $e_q(t\mathrm{J})$ in the same way as T is a "box" of J. Consequently, from (4.5) we learn that the general solution will be a linear combination of

$$e_q[x(1-q)a_i],\ xe_q'[x(1-q)a_i],\ \ldots,\ x^{k-1}e_q^{(k_i-1)}[x(1-q)a_i]$$

where the a_i are the eigenvalues of A belonging to different elementary divisors and the k_i the corresponding orders. We see that the solution has an analogous shape as the solution of a linear differential equation, the exponential functions having been replaced by $e_q(t)$ and its derivatives. But because $e_q(t)$ is a meromorphic function the solution of (4.4) will be a meromorphic function also whereas the solution of a linear differential equation with constant coefficients is an entire function.

5. *The Singular Case.*—Now let us weaken the assumption that $y(0)$ will be a constant finite vector, different from zero. We are restricting ourselves to the homogeneous case. We consider the equation in the more general form [*cf.* (1.6)]

$$y(qx) = \mathrm{B}(x)\,y(x) \tag{5.1}$$

and assume that $\mathrm{B}(x)$ may be bounded and that

$$\mathrm{B}(0) = \mathrm{C}\ (\det \mathrm{C} \neq 0). \tag{5.2}$$

Without loss of generality we may assume that C is given in its canonical form otherwise we may apply a linear transformation like (4.2). Now we write

$$y(qx) = [\mathrm{C} + x\mathrm{D}(x)]\,y(x) \tag{5.3}$$

and introduce τ by

$$x = q^{\tau} \quad \text{or} \quad \tau = \frac{\log x}{\log q}. \tag{5.4}$$

Let the matrix T given by (4.6) be one of the "boxes" of C and let

$$a = q^{\alpha}$$

The matrix

$$\mathrm{N}_a(x) = \begin{pmatrix} x^{\alpha} & x^{\alpha}q^{-\alpha}\binom{\tau}{1} & x^{\alpha}q^{-2\alpha}\binom{\tau}{2} & \ldots & x^{\alpha}q^{(1-k)\alpha}\binom{\tau}{k-1} \\ 0 & x^{\alpha} & x^{\alpha}q^{-\alpha}\binom{\tau}{1} & \ldots & x^{\alpha}q^{(2-k)\alpha}\binom{\tau}{k-2} \\ \cdot & \cdot & \cdot & \ldots & \cdot \\ 0 & 0 & 0 & \ldots & x^{\alpha} \end{pmatrix} \tag{5.4}$$

satisfies the geometrical difference equation

$$N_\alpha(qx) = TN_\alpha(x) \tag{5.5}$$

which may be verified easily. Composing the different "boxes" N_α to a matrix N of the order n we find that N will satisfy the equation

$$N(qx) = CN(x). \tag{5.6}$$

Now we set

$$y(x) = N(x)\,u(x). \tag{5.7}$$

Then $u(x)$ will satisfy the equation

$$u(qx) = (I + xN^{-1}C^{-1}DN)\,u(x) \tag{5.8}$$

which is of the special type considered in 2 if the matrix $G = xN^{-1}C^{-1}DN$ is bounded. But this condition is not fulfilled at any rate because the elements of G contain powers of x multiplied into powers of $\log x$. A sufficient condition for boundness will be that all the occurring powers of x have an exponent larger than zero. If $a_1, \ldots, a_p$ are the eigenvalues of C and if $c_i = q^{\alpha_i}$, then the exponents which occur in N will be $\alpha_1, \ldots, \alpha_p$, and the above-mentioned condition may be written as

$$1 + \alpha_i - \alpha_j > 0\,(i, j = 1, \ldots, p)$$

or

$$-\tfrac{1}{2} \leqslant \alpha_i \leq +\tfrac{1}{2}. \tag{5.9}$$

If it is fulfilled the equation (5.8) can be resolved, $u(0)$ being finite. Considering (5.7) we see that the solution $y(x)$ will be weakly singular in the neighbourhood of the origin.

If $\det C = 0$ the equation (5.8) has no meaning, and the discussed method cannot be applied. In this case, some of the components of $y(x)$ will be strongly singular at $x = 0$.

6. *Exceptional Points.*—In the above reflections, the point $x = 0$ was treated as an exceptional point in which the solutions may get singularities. Now, every geometrical difference equation has at least one more exceptional point and that is $x = \infty$. Substituting $\xi = x^{-1}$ we get an equation for $y(\xi^{-1}) = \eta(\xi)$ which has the origin as its exceptional point, and so we have the former case. Sometimes it happens that $x = 0$ will be a strong singularity whereas $x = \infty$ will be a weak one.

In the regular case we can solve the equation (2.1) also for given initial values $y(a)$, $a \neq 0$, provided that a is situated within the circle of convergence of (2.4). In fact, we have

$$y(a) = \mathrm{F}[\mathrm{A}(a),\ a(1-q)]\, y(0) \tag{6.1}$$

and by eliminating $y(0)$ from (2.3) and (6.1) we find

$$y(x) = \mathrm{F}[\mathrm{A}(x),\ x(1-q)]\ [\mathrm{F}\{\mathrm{A}(a),\ a(1-q)\}]^{-1}\, y(a). \tag{6.2}$$

References

1. Trjitzinsky, W. J. .. "Analytical theory of linear q-difference equations," *Acta math.*, 1931, **61**, 1–38.

2. Hahn, W. .. "Beiträge zur Theorie der Heineschen Reihen," *Math. Nachr.*, 1949, **2**, 340–79.

INTENSITY STUDIES IN RAMAN EFFECT: EFFECT OF CONJUGATION

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The C = O stretching frequency in the case of normal ketones, aldehydes and esters, occurs at fairly constant position both in Raman effect and infra-red.[1,2] The carbonyl frequency is determined by the nature of its immediate environment. The infra-red studies by Cross and Rolfe[3] on some ketones show that there is an increase in frequency of the C = O line with non-polar solvents and a decrease with polar solvents. Their results show that the factors which influenee the frequency of the carbonyl absorption also influence its characteristic intensity.

Jesef Goubeau and Ruth Deerdt,[4] from the study of the influence of solvents on the Raman lines of some ketones, have shown that there is a change in frequency of all the lines, especially the C = O line. There is an increase in frequency with non-polar solvents and polar halides, while the other solvents have produced a decrease.

The present investigation was undertaken to study the influence of various solvents on the frequencies and the intensities of the Raman lines in various unconjugated and conjugated substances.

Experimental

Extra pure samples of the substances distilled at constant boiling points have been used in the present investigation. A Hilger E 612 two-prism glass spectrograph, in conjunction with a Hilger Raman Source Unit was used. The spectra of the various substances have been recorded under identical conditions. A set of graded intensity marks were also given on the same plate and the intensities were computed using a Moll microphotometer.

Results

The mixtures used are 50% by volume. The intensity values given in the accompanying Tables I to IV are the ratios of the integrated intensities of the various lines to the integrated intensity of 458 cm.$^{-1}$ line of CCl_4. Table V contains the values of C = O frequency in various substances in both pure and solution states.

TABLE I

C = O Frequency

Substance \ Solvent	Pure	CS_2	CCl_4	C_6H_{12}	$CHCl_3$	C_6H_6	Dioxan
Methyl ethyl ketone	0·064	..	..	0·054	..	0·035	..
Ethyl acrylate	..	..	..	0·073	..	0·028	..
Benzaldehyde	4·540	9·900	0·669	0·344	1·242	0·739	1·820
Acetophenone	1·153	2·380	0·445	0·175	0·596	0·260	..
Benzophenone	..	2·390	0·360	..	0·779	0·277	0·786
Phenyl acetate	0·169	0·208	0·092	0·034	..	..	0·021

TABLE II

C = C Frequency

Substance \ Solvent	Pure	CS_2	CCl_4	$CHCl_3$	Dioxan
Benzaldehyde	3·472	9·615	0·625	1·477	1·095
Acetophenone	1·071	3·674	0·487	0·679	..
Benzophenone	..	4·019	0·474	0·795	1·226
Phenyl acetate	0·215	0·436	0·088	..	..

TABLE III

$C - H_{arom}$ Frequency

Substance \ Solvent	Pure	CS_2	CCl_4	$CHCl_3$	Dioxan
Benzaldehyde	1·520	1·449	..	0·489	0·601
Benzophenone	..	0·973	0·269	0·455	0·530
Acetophenone	0·407	1·157	0·305	..	..
Phenyl acetate	0·256	1·610	..	..	0·311

TABLE IV

C — C Frequency

Substance \ Solvent	Pure	CS_2	CCl_4	$CHCl_3$	Dioxan
Benzaldehyde	3·113	3·210	0·364	0·569	0·687
Acetophenone	0·936	1·633	0·679	0·332	..
Benzophenone	..	1·924	0·215	0·455	1·40
Phenyl acetate	0·759	1·811	0·163	..	0·780

TABLE V

Frequency of C = O Vibration (cm.$^{-1}$)

Substance \ Solvent	Pure	CS_2	CCl_4	$CHCl_3$	C_6H_6	C_6H_{12}	Dioxan
Ethyl acrylate	1720·0	1727·8	1725·0	..	..	1730·0	..
Acetophenone	1680·0	1690·4	1687·0	1680·9	1691·3	1673·3	1681·8
Benzophenone	1660·0	1665·2	1665·2	1659·7	1664·2	1662·7	1661·9
Benzaldehyde	1700·0	1704·0	1705·0	1700·8	1708·5	1709·0	1701·7

DISCUSSION

The following conclusions can be drawn from the results given in the above tables:—

(1) The frequency of the C = O line shows, in general, an increase in the non-polar solvents and no appreciable change in $CHCl_3$ solution. This observation is in agreement with Goubeau and Deerdt so far as the non-polar solvents are concerned; but in the case of polar halides they have recorded an increase while there is no change in the present investigation. The C = C, C – C frequencies do not show appreciable variation.

(2) The intensity of the C = O line in the unconjugated methyl ethyl ketone does not show any appreciable variation in different solvents.

(3) The intensity of the C = O line in the conjugated aromatic compounds is high compared to that in the unconjugated or conjugated aliphatic compounds even in the solution state.

(4) The intensity of the C = O line in CS_2 solution is found to be considerably increased whereas in other solvents an appreciable diminution is noticed. This diminution is more marked in non-polar solvents.

In the case of phenyl acetate, where there is conjugation of C = C with the benzene ring through the oxygen atom, the intensity of the lines is very small compared to the other conjugated aromatic compounds. In

this case also the intensity of the C = O line has been considerably increased in CS_2 solution.

The behaviour of the C = C, C – C and C – H_{arom} vibrations is quite similar to the C = O vibration.

SUMMARY

The changes in frequency and the intensities of the various unconjugated and conjugated substances in different solvents have been investigated. It is found that there is an increase in C = O frequency in non-polar solvents. The intensity of the C = O line shows in general, considerable diminution in non-polar solvents. The C = C, C – H_{arom} and C – C vibrations also behave in the same way.

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REFERENCES

1. Hibben, J. H. .. *The Raman Effect and Its Chemical Applications*, Reinhold, 1939.
2. Bellamy, L. J. .. *The Infra-red Spectra of Complex Molecules*, Methuen, 1956.
3. Cross, L. H. and Rolfe, A. C. *Trans. Farad. Soc.*, 1951, **47**, 354.
4. Jesef Goubeau, P. and Ruth Deerdt *Naturwissenschaften*, 1948, **35**, 93.

INTENSITY OF RAMAN LINES IN CARBOXYLIC ACIDS, ESTERS AND NITRILES

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A good deal of work has been done in both Raman effect[1-2] and infra-red[3-4] on the assignment of characteristic frequencies in carbonyl compounds and nitriles. In majority of cases the Raman and infra-red frequencies are very nearly the same although occasionally large differences are also observed. In the infra-red, some work has been done on the intensity of carbonyl absorption[5-6] of carboxylic acids and also of nitrile absorption[5,7] but very little work has been done in Raman effect.

In the present investigation, the intensities of the characteristic bonds of type C = O, C – H bending, C – H_{ailph} stretching, C – C and C ≡ N whose frequencies lie in the region 1700, 1400, 2900, 800 and 2300 cm.$^{-1}$ respectively, have been studied.

Experimental

Extra pure samples of the substances distilled at constant boiling-points have been used in the present investigation. A Hilger E 612 two-prism glass spectrograph in conjunction with a Hilger Raman Source Unit was used. The spectra of various substances have been recorded under identical conditions. A set of graded intensity marks were also given on the same plate and the intensities were computed using a Moll Microphotometer. The intensity values obtained have been reduced to standard intensity values (S) by making use of the expression suggested by Bernstein and Allen.[8]

Results

Table I

Carboxylic acids

Substance	Nature of vibration	Frequency cm.$^{-1}$	$I/I_{488\ CCl_4}$	Standard intensity (S)
Acetic acid ..	C = O	1669	0·063	0·151
Propionic acid ..		1669	0·073	0·233
Butyric acid ..		1670	0·107	0·434

TABLE I—(*Contd.*)

Substance	Name of vibration	Frequency cm.$^{-1}$	$I/I_{458\ cc14}$	Standard intensity (S)
Acetic acid ..	C — H bending	1435	0·124	0·242
Propionic acid ..		1448	0·207	0·552
Valeric acid ..		1430	0·171	0·690
Acetic acid ..	$C - H_{aliph}$	2934	0·211	1·131
Propionic acid ..		2956	0·354	2·576
Butyric acid ..		2944	0·329	3·009
Valeric acid ..		2956	0·484	5·416
Acetic acid ..	C — C	895	0·325	0·355
Propionic acid ..		842	0·232	0·316
Valeric acid ..		826	0·144	0·295

TABLE II

Carboxylic esters

Substance	Nature of vibration	Frequency cm.$^{-1}$	$I/I_{458\ cc14}$	Standard intensity (S)
Methyl butyrate ..	C = O	1740	0·104	0·540
Ethyl butyrate ..		1739	0·171	1·025
Methyl acetate ..	C — H bending	1455	0·201	0·601
Amyl acetate ..		1452	0·270	1·471
Methyl butyrate ..		1453	0·230	0·942
Ethyl butyrate ..		1455	0·234	1·111
Methyl acetate ..	$C - H_{aliph}$	2942	0·163	1·314
Ethyl acetate ..		2940	0·183	1·663
Amyl acetate ..		2940	0·256	3·761
Methyl butyrate ..		2940	0·443	4·902
Ethyl butyrate ..		2941	0·486	6·242
Methyl acetate ..	C — C	646	0·161	0·176
Ethyl acetate ..		633	0·125	0·151
Amyl acetate ..		620	0·072	0·136

TABLE III

Nitriles

Substance	Nature of vibration	Frequency cm.$^{-1}$	$I/I_{488\ cc_4}$	Standard intensity (S)
Aceto nitrile ..	C ≡ N	2250	0·282	0·852
Propio nitrile ..		2245	0·175	0·750
Butyro nitrile ..		2244	0·092	0·511
Benzo nitrile ..		2224	2·119	17·440

DISCUSSION

From Tables I and II the following general conclusions regarding the characteristic vibrations in both carboxylic acids and esters may be arrived at:

(1) The intensity of the lines due to C = O vibration is found to increase as we go from lower to higher members of the series.

(2) The intensities of lines in the regions 1400 cm.$^{-1}$ and 2900 cm.$^{-1}$ characteristic of C — H bending and C — H_{aliph} stretching vibrations also behave in the same way as in (1).

(3) The addition of a CH_2 group in a homologous series has a different effect on the low frequency region characteristic of C — C vibration in the sense that the intensities show a gradual decrease from lower to higher members of the series.

From Table III it can be seen that (1) the intensity of the line due to C ≡ N vibration is found to be decreasing from the lower to the higher members of the homologous series. This conclusion is in agreement with the observation in the infra-red.[7] (2) The large intensity in aromatic conjugated substance of benzo nitrile compared to the aliphatic unconjugated nitriles may be explained as due to the combined effect of the general increase in intensity to be expected from aliphatic to aromatic and also from unconjugated to conjugated substances.[9–10] This observation is in conformity with that made by Cross and Rolfe[5] in infra-red absorption.

SUMMARY

The intensities of characteristic vibrations in carboxylic acids, esters and nitriles have been studied. In both carboxylic acids and esters the intensities of Raman lines due to C = O, C – H bending and C – H_{aliph} stretching vibrations are found to increase from lower to higher members of the series while there is a decrease in intensity of C – C frequency. The intensity of the lines due to C ≡ N vibration is found to be decreasing from lower to higher members of the series. The intensity in aromatic conjugated nitrile is found to be abnormally great when compared to that in unconjugated aliphatic nitriles.

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REFERENCES

1. Hibben, H. J. .. *The Raman Effect and Its Chemical Applications*, Rainhold, New York, 1939.
2. Landolt Bornstein .. *Roth/Scheel Physikalisch = Chemische Tabellen*, Zweiter Teil, 1935.
3. Bellamy, L. J. .. *The Infra-red Spectra of Complex Molecules*, Methuen & Co., Ltd., London, 1956.
4. West, W. .. *Chemical Applications of Spectroscopy*, Interscience Publishers, Inc., New York, 1956.
5. Cross, L. H. and Rolfe, A. C. *Trans. Farad. Soc.*, 1951, **47**, 354.
6. Flett, M. St. C. .. *J. Chem. Soc.*, 1951, 962.
7. Kitson, R. E. and Griffith, N. E. *Analyt. Chem.*, 1952, **24**, 334.
8. Bernstein, H. J. and Allen, G. *J. Opt. Soc. Amer.*, 1955, **45**, 237.
9. Venkateswarlu, K. and Thyagarajan, G. *Z. Physik.*, 1959, **154**, 70.
10. ———— .. *Ibid.*, 1959, **156**, 561.

SUPERPOSABILITY OF STEADY AXI-SYMMETRICAL FLOWS IN A NON-NEWTONIAN FLUID

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Let (q_1, p_1, Ω_1) and (q_2, p_2, Ω_2) be the two flows of an incompressible fluid of uniform density ρ, kinematic viscosity ν and kinematic cross-viscosity ν_c, where q, p, Ω denote the velocity vector, the presssure and the potential from which the external forces are assumed to be derived. The two flows are said to be superposable, if a pressure $(p_1 + p_2 + \pi)$ can be found such that $(q_1 + q_2, p_1 + p_2 + \pi, \Omega_1 + \Omega_2)$ is also a solution of the Stokes-Navier equation with the necessary modification in the initial and boundary conditions.

The equations of motion for a non-Newtonian fluid are given by,

$$\rho\left(\frac{\partial u_i}{\partial t} + u_{i,j}u_j\right) = t^i{}_{j,j} + f^i, \tag{0.1}$$

$$u_{j,j} = 0 \tag{0.2}$$

$t_j{}^i$ being the stress tensor given by

$$t_j{}^i = -p\delta_j{}^i + F_1 d_j{}^i + F_2 d_a{}^i d_j{}^a, \tag{0.3}$$

where f^i is the body force,

$$d_j{}^i = u_{j,i} + u_{i,j} \tag{0.4}$$

is the rate of deformation tensor, F_1 and F_2 are functions of some material constants and the second and third invariants of the rate of deformation tensor $d_j{}^i$.

By taking $F_1 = \mu$ and $F_2 = \mu_c$ we recognize F_1 and F_2 to be the coefficient of viscosity and coefficient of cross-viscosity.

1. For the problem on hand it is convenient to use cylindrical co-ordinate system (r, θ, Z) in which z-axis is taken to be the axis of symmetry and r is the distance from the axis. The velocity components at any point

are given by u_r, u_θ and u_z, where the velocity vector q does not necessarily lie in the meridian plane, so that

$$q = u_r i_r + u_\theta i_\theta + u_z i_z,$$

where for axial-symmetry the velocity components are functions of r and z only besides the time t.

(*a*) *Equations of motion.*—The equations of steady motion in cylindrical co-ordinates, with terms of azimuthal variation neglected, are,

$$\rho\left(u_r \frac{\partial u_r}{\partial r} + u_z \frac{\partial u_r}{\partial z} - \frac{u_\theta^2}{r}\right) = \frac{\partial P_{rr}}{\partial r} + \frac{\partial P_{rz}}{\partial z} + \frac{P_{rr} - P_{\theta\theta}}{r}, \tag{1.1}$$

$$\rho\left(u_r \frac{\partial u_\theta}{\partial r} + u_z \frac{\partial u_\theta}{\partial z} + \frac{u_r u_\theta}{r}\right) = \frac{\partial P_{r\theta}}{\partial r} + \frac{\partial P_{\theta z}}{\partial z} + \frac{2P_{r\theta}}{r}, \tag{1.2}$$

$$\rho\left(u_r \frac{\partial u_z}{\partial r} + u_z \frac{\partial u_z}{\partial z}\right) = \frac{\partial P_{rz}}{\partial r} + \frac{\partial P_{zz}}{\partial z} + \frac{P_{rz}}{r}, \tag{1.3}$$

along with the equation of continuity

$$\frac{\partial u_r}{\partial r} + \frac{u_r}{r} + \frac{\partial u_z}{\partial z} = 0, \tag{1.4}$$

where the stress matrix P_{ij} and the rate of strain matrix e_{ij} in the case of non-Newtonian fluids are related as (Braun and Reiner[1])

$$\begin{pmatrix} P_{rr} & P_{r\theta} & P_{rz} \\ P_{\theta r} & P_{\theta\theta} & P_{\theta z} \\ P_{zr} & P_{z\theta} & P_{zz} \end{pmatrix} = -p \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \mu \begin{pmatrix} e_{rr} & e_{r\theta} & e_{rz} \\ e_{\theta r} & e_{\theta\theta} & e_{\theta z} \\ e_{zr} & e_{z\theta} & e_{zz} \end{pmatrix}$$

$$+ \mu_c \begin{pmatrix} e_{rr} & e_{r\theta} & e_{rz} \\ e_{\theta r} & e_{\theta\theta} & e_{\theta z} \\ e_{zr} & e_{z\theta} & e_{zz} \end{pmatrix} \begin{pmatrix} e_{rr} & e_{r\theta} & e_{rz} \\ e_{\theta r} & e_{\theta\theta} & e_{\theta z} \\ e_{zr} & e_{z\theta} & e_{zz} \end{pmatrix}, \tag{1.5}$$

where $e_{ij} = e_{ji}$

$$\left.\begin{aligned} e_{rr} &= 2\frac{\partial u_r}{\partial r} & e_{r\theta} &= \frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r} \\ e_{\theta\theta} &= 2\frac{u_r}{r} & e_{rz} &= \frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r} \\ e_{zz} &= 2\frac{\partial u_z}{\partial z} & e_{\theta z} &= \frac{\partial u_\theta}{\partial z} \end{aligned}\right\}. \tag{1.6}$$

Using the relations (1.4), (1.5) and (1.6), the equations of motion (1.1), (1.2) and (1.3) for axially symmetric steady flow become,

$$u_r \frac{\partial u_r}{\partial r} + u_z \frac{\partial u_r}{\partial z} - \frac{u_\theta^2}{r}$$

$$= -\frac{1}{\rho}\frac{\partial p}{\partial r} + \nu\left(\nabla^2 u_r - \frac{u_r}{r^2}\right) + 2\nu_c \left\{4\frac{\partial u_r}{\partial r}\cdot\frac{\partial^2 u_r}{\partial r^2}\right.$$

$$+ \left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}\right)\left(\frac{\partial^2 u_r}{\partial r \partial z} + \frac{\partial^2 u_z}{\partial r^2}\right) - \frac{u_r}{r}\frac{\partial^2 u_z}{\partial r \partial z} - \frac{u_r}{r}\frac{\partial^2 u_r}{\partial z^2}$$

$$\left. - \frac{1}{2r}\left(\frac{\partial u_r}{\partial z}\right)^2 + \frac{1}{2r}\left(\frac{\partial u_z}{\partial r}\right)^2 + \frac{2}{r}\left(\frac{\partial u_r}{\partial r}\right)^2 - \frac{2u_r^2}{r^3}\right\}$$

$$+ \nu_c \left\{2\left(\frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r}\right)\frac{\partial}{\partial r}\left(\frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r}\right) + \frac{\partial u_\theta}{\partial z}\frac{\partial}{\partial z}\left(\frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r}\right)\right.$$

$$\left. - \frac{1}{r}\left(\frac{\partial u_\theta}{\partial z}\right)^2 + \left(\frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r}\right)\frac{\partial^2 u_\theta}{\partial z^2}\right\}, \qquad (1.1\,a)$$

$$u_r \frac{\partial u_\theta}{\partial r} + u_z \frac{\partial u_\theta}{\partial z} + \frac{u_r u_\theta}{r}$$

$$= -\frac{1}{\rho}\frac{\partial p}{\partial \theta} + \nu\left(\nabla^2 u_\theta - \frac{u_\theta}{r^2}\right) + \nu_c \left\{\frac{\partial^2 u_\theta}{\partial r \partial z}\left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}\right)\right.$$

$$+ \frac{\partial u_\theta}{\partial z}\frac{\partial}{\partial r}\left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}\right) - 2\frac{\partial^2 u_r}{\partial r \partial z}\frac{\partial u_\theta}{\partial z} + \left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}\right)$$

$$\times \frac{\partial}{\partial z}\left(\frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r}\right) + \left(\frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r}\right)\frac{\partial}{\partial z}\left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}\right)$$

$$- 2\frac{\partial u_z}{\partial z}\frac{\partial}{\partial r}\left(\frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r}\right) - 2\frac{\partial^2 u_\theta}{\partial z^2}\frac{\partial u_r}{\partial r}$$

$$- 2\frac{\partial^2 u_z}{\partial r \partial z}\left(\frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r}\right) - \frac{4}{r}\frac{\partial u_z}{\partial z}\left(\frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r}\right)$$

$$\left. + \frac{2}{r}\left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}\right)\frac{\partial u_\theta}{\partial z}\right\}, \qquad (1.2\,a)$$

and

$$u_r \frac{\partial u_z}{\partial r} + u_z \frac{\partial u_z}{\partial z}$$

$$= -\frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\nabla^2 u_z + 2\nu_c \left\{4\frac{\partial u_z}{\partial z}\cdot\frac{\partial^2 u_z}{\partial z^2} - \frac{u_r}{r}\frac{\partial^2 u_r}{\partial r \partial z}\right.$$

$$+ \left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}\right)\left(\frac{\partial^2 u_r}{\partial z^2} + \frac{\partial^2 u_z}{\partial r \partial z}\right) - \frac{u_r}{r}\frac{\partial u^2 z}{\partial r^2}$$

$$\left. - \frac{1}{r}\frac{\partial u_r}{\partial r}\cdot\frac{\partial u_r}{\partial z} - \frac{1}{r}\frac{\partial u_r}{\partial r}\cdot\frac{\partial u_z}{\partial r}\right\} + \nu_c \left\{\frac{\partial u_\theta}{\partial z}\left(2\frac{\partial^2 u_\theta}{\partial z^2} + \frac{\partial^2 u_\theta}{\partial r^2}\right)\right.$$

$$\left. + \frac{\partial^2 u_\theta}{\partial r \partial z}\left(\frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r}\right)\right\}. \qquad (1.3\,a)$$

Expressing the velocity components in terms of the Stokes' stream function ψ, we have

$$u_r = \frac{1}{r}\frac{\partial \psi}{\partial z}, \quad u_\theta = \chi(r, z), \quad u_z = -\frac{1}{r}\frac{\partial \psi}{\partial r},$$

i.e.,

$$\boldsymbol{q} = \left(\frac{1}{r}\frac{\partial \psi}{\partial z}\right)\boldsymbol{i}_r + \chi \boldsymbol{i}_\theta + \left(-\frac{1}{r}\frac{\partial \psi}{\partial r}\right)\boldsymbol{i}_z. \tag{1.7}$$

(*b*) *The conditions of integrability*.—The conditions of integrability of the equations of motion in terms of the Stokes' stream function ψ turn out to be,

$$\begin{aligned} & r\mathrm{J}\begin{pmatrix}\psi & r^{-2}\mathrm{E}^2\psi \\ z & r\end{pmatrix} - 2\chi\frac{\partial \chi}{\partial z} \\ & = \nu \mathrm{E}^4\psi + 2\nu_c\left\{\frac{2}{r}\mathrm{J}\begin{pmatrix}\psi & r^{-2}\mathrm{E}^2\psi \\ z & r\end{pmatrix} - 2\mathrm{J}\begin{pmatrix}\frac{\partial \psi}{\partial r} & r^{-2}\mathrm{E}^2\psi \\ z & r\end{pmatrix}\right. \\ & \quad \left. - \frac{\partial}{\partial z}\left(\frac{1}{r}\mathrm{E}^2\psi\right)^2 - \frac{1}{r^2}\frac{\partial \psi}{\partial z}\mathrm{E}^4\psi + \frac{2}{r}\frac{\partial \psi}{\partial z}\frac{\partial}{\partial r}\left(\frac{\mathrm{E}^2\psi}{r^2}\right)\right\} \\ & \quad + \nu_c\left\{r^2\mathrm{J}\begin{pmatrix}\mathrm{E}^2\chi & \frac{\chi}{r} \\ z & r\end{pmatrix} - 2r\mathrm{J}\begin{pmatrix}\frac{\partial \chi}{\partial r} & \frac{\chi}{r} \\ z & r\end{pmatrix} - \frac{3\chi}{r^2}\frac{\partial \chi}{\partial z}\right. \\ & \quad \left. - 5\frac{\partial \chi}{\partial z}\mathrm{E}^2\chi\right\} \end{aligned} \tag{1.8}$$

and

$$\begin{aligned} & \frac{1}{r^2}\mathrm{J}\begin{pmatrix}\psi & r\chi \\ z & r\end{pmatrix} \\ & = \nu\left(\nabla^2\chi - \frac{\chi}{r^2}\right) + \nu_c\left\{\mathrm{J}\begin{pmatrix}\nabla^2\psi & \frac{\chi}{r} \\ z & r\end{pmatrix} + \frac{2}{r}\mathrm{J}\begin{pmatrix}\frac{\partial \psi}{\partial z} & \frac{\partial \chi}{\partial z} \\ z & r\end{pmatrix}\right. \\ & \quad \left. + \frac{2}{r}\mathrm{J}\begin{pmatrix}\frac{\partial \psi}{\partial r} & \frac{\partial \chi}{\partial r} \\ z & r\end{pmatrix} + \frac{2}{r^2}\frac{\partial \psi}{\partial r}\frac{\partial^2 \chi}{\partial r \partial z} + \frac{2}{r^2}\frac{\partial \psi}{\partial z}\frac{\partial^2 \chi}{\partial z^2}\right\}, \end{aligned} \tag{1.9}$$

where

$$\mathrm{E}^2 \equiv \frac{\partial^2}{\partial r^2} + \frac{\partial^2}{\partial z^2} - \frac{1}{r}\frac{\partial}{\partial r}$$

and

$$\nabla^2 \equiv \frac{\partial^2}{\partial r^2} + \frac{\partial^2}{\partial z^2} + \frac{1}{r}\frac{\partial}{\partial r}.$$

(*c*) *Conditions for superposability of two motions.*—Taking the two motions given by

$$\boldsymbol{q}_s = \left(\frac{1}{r}\frac{\partial \psi_s}{\partial z}\right)\boldsymbol{i}_r + \chi_s \boldsymbol{i}_\theta + \left(-\frac{1}{r}\frac{\partial \psi_s}{\partial r}\right)\boldsymbol{i}_z$$

where $s = 1, 2$ corresponds to two motions. Using the conditions of integrability (1.8) and (1.9), we obtain the following conditions for superposability of two motions:

$$\begin{aligned}
&r\mathrm{J}\begin{pmatrix}\psi_1 & r^{-2}\mathrm{E}^2\psi_2\\ z & r\end{pmatrix} + r\mathrm{J}\begin{pmatrix}\psi_2 & r^{-2}\mathrm{E}^2\psi_1\\ z & r\end{pmatrix} - 2\chi_1\frac{\partial \chi_2}{\partial z} - 2\chi_2\frac{\partial \chi_1}{\partial z}\\
&\quad = 2\nu_c\left\{\frac{2}{r}\mathrm{J}\begin{pmatrix}\psi_1 & r^{-2}\mathrm{E}^2\psi_2\\ z & r\end{pmatrix} + \frac{2}{r}\mathrm{J}\begin{pmatrix}\psi_2 & r^{-2}\mathrm{E}^2\psi_1\\ z & r\end{pmatrix}\right.\\
&\qquad - 2\mathrm{J}\begin{pmatrix}\frac{\partial \psi_1}{\partial r} & r^{-2}\mathrm{E}^2\psi_2\\ z & r\end{pmatrix} - 2\mathrm{J}\begin{pmatrix}\frac{\partial \psi_2}{\partial r} & r^{-2}\mathrm{E}^2\psi_1\\ z & r\end{pmatrix}\\
&\qquad + \frac{2}{r}\frac{\partial \psi_1}{\partial z}\frac{\partial}{\partial r}\left(\frac{\mathrm{E}^2\psi_2}{r^2}\right) + \frac{2}{r}\frac{\partial \psi_2}{\partial z}\frac{\partial}{\partial r}\left(\frac{\mathrm{E}^2\psi_1}{r^2}\right) - \frac{1}{r^2}\frac{\partial \psi_1}{\partial z}\mathrm{E}^4\psi_2\\
&\qquad \left. - \frac{1}{r^2}\frac{\partial \psi_2}{\partial z}\mathrm{E}^4\psi_1\right\} + \nu_c\left\{r^2\mathrm{J}\begin{pmatrix}\mathrm{E}^2\chi_1 & \frac{\chi_2}{r}\\ z & r\end{pmatrix} + r^2\mathrm{J}\begin{pmatrix}\mathrm{E}^2\chi_2 & \frac{\chi_1}{r}\\ z & r\end{pmatrix}\right.\\
&\qquad - 2r\mathrm{J}\begin{pmatrix}\frac{\partial \chi_1}{\partial r} & \frac{\chi_2}{r}\\ z & r\end{pmatrix} - 2r\mathrm{J}\begin{pmatrix}\frac{\partial \chi_2}{\partial r} & \frac{\chi_1}{r}\\ z & r\end{pmatrix} - \frac{3\chi_1}{r^2}\frac{\partial \chi_2}{\partial z}\\
&\qquad \left. - 3\frac{\chi_2}{r^2}\frac{\partial \chi_1}{\partial z} - 5\frac{\partial \chi_1}{\partial z}\mathrm{E}^2\chi_2 - 5\frac{\partial \chi_2}{\partial z}\mathrm{E}^2\chi_1\right\} \qquad (1.10)
\end{aligned}$$

and

$$\begin{aligned}
&\mathrm{J}\begin{pmatrix}\psi_1 & r\chi_2\\ z & r\end{pmatrix} + \mathrm{J}\begin{pmatrix}\psi_2 & r\chi_1\\ z & r\end{pmatrix}\\
&\quad = \frac{\nu_c}{r}\left\{\mathrm{J}\begin{pmatrix}\nabla^2\psi_1 & \frac{\chi_2}{r}\\ z & r\end{pmatrix} + \mathrm{J}\begin{pmatrix}\nabla^2\psi_2 & \frac{\chi_1}{r}\\ z & r\end{pmatrix} + 2\mathrm{J}\begin{pmatrix}\frac{\partial \psi_1}{\partial z} & \frac{\partial \chi_2}{\partial z}\\ z & r\end{pmatrix}\right.
\end{aligned}$$

$$+ 2\mathrm{J}\begin{pmatrix} \frac{\partial \psi_2}{\partial z} & \frac{\partial \chi_1}{\partial z} \\ z & r \end{pmatrix} + 2\mathrm{J}\begin{pmatrix} \frac{\partial \psi_1}{\partial r} & \frac{\partial \chi_2}{\partial r} \\ z & r \end{pmatrix} + 2\mathrm{J}\begin{pmatrix} \frac{\partial \psi_2}{\partial r} & \frac{\partial \chi_1}{\partial r} \\ z & r \end{pmatrix}$$

$$+ \frac{2}{r}\frac{\partial \psi_1}{\partial r}\frac{\partial^2 \chi_2}{\partial r \partial z} + \frac{2}{r}\frac{\partial \psi_2}{\partial r}\frac{\partial^2 \chi_1}{\partial r \partial z} + \frac{2}{r}\frac{\partial \psi_1}{\partial z}\frac{\partial^2 \chi_2}{\partial z^2} + \frac{2}{r}\frac{\partial \psi_2}{\partial z}\frac{\partial^2 \chi_1}{\partial z^2}\Big\}. \tag{1.11}$$

We can easily show that the conditions (1.10) and (1.11) are both necessary and sufficient for the two axially symmetric flows of a non-Newtonian fluid corresponding to the two stream functions ψ_1 and ψ_2 to be superposable.

2. CONDITIONS FOR SELF-SUPERPOSABILITY OF A FLOW:

Using the conditions (1.10) and (1.11), it follows that the flow with stream function ψ is self-superposable if and only if,

$$r\mathrm{J}\begin{pmatrix} \psi & r^{-2}\mathrm{E}^2\psi \\ z & r \end{pmatrix} - 2\chi\frac{\partial \chi}{\partial z}$$

$$= 2\nu_c\left[\frac{2}{r}\mathrm{J}\begin{pmatrix} \psi & r^{-2}\mathrm{E}^2\psi \\ z & r \end{pmatrix} - 2\mathrm{J}\begin{pmatrix} \frac{\partial \psi}{\partial r} & r^{-2}\mathrm{E}^2\psi \\ z & r \end{pmatrix} + \frac{2}{r}\frac{\partial \psi}{\partial z}\frac{\partial}{\partial r}\left(\frac{\mathrm{E}^2\psi}{r^2}\right)\right.$$

$$\left. - \frac{1}{r^2}\frac{\partial \psi}{\partial z}\mathrm{E}^4\psi\right] + \nu_c\left[r^2\mathrm{J}\begin{pmatrix} \mathrm{E}^2\chi & \frac{\chi}{r} \\ z & r \end{pmatrix} - 2\mathrm{J}\begin{pmatrix} \frac{\partial \chi}{\partial r} & \frac{\chi}{r} \\ z & r \end{pmatrix}\right.$$

$$\left. - \frac{3\chi}{r^2}\frac{\partial \chi}{\partial z} - 5\frac{\partial \chi}{\partial z}\mathrm{E}^2\chi\right] \tag{2.1}$$

and

$$\mathrm{J}\begin{pmatrix} \psi & r\chi \\ z & r \end{pmatrix} = \frac{\nu_c}{r}\left[\mathrm{J}\begin{pmatrix} \nabla^2\psi & \frac{\chi}{r} \\ z & r \end{pmatrix} + 2\mathrm{J}\begin{pmatrix} \frac{\partial \psi}{\partial z} & \frac{\partial \chi}{\partial z} \\ z & r \end{pmatrix} + 2\mathrm{J}\begin{pmatrix} \frac{\partial \psi}{\partial r} & \frac{\partial \chi}{\partial r} \\ z & r \end{pmatrix}\right.$$

$$\left. + \frac{2}{r}\frac{\partial \psi}{\partial r}\frac{\partial^2 \chi}{\partial r \partial z} + \frac{2}{r}\frac{\partial \psi}{\partial z}\frac{\partial^2 \chi}{\partial z^2}\right]. \tag{2.2}$$

3. PARTICULAR CASES

(*a*) *Newtonian fluids.*—If in the conditions of superposability and self-superposability by putting $\nu_c = 0$, we obtain the conditions of superposability

and self-superposability for a Newtonian fluid as obtained by Lakshmana Rao.[3]

(*b*) *Velocity vector lies in the meridian plane.*—We can find the conditions of superposability and self-superposability in steady axi-symmetrical flows when the velocity vector $\boldsymbol{q}$ lies in the meridian plane,

i.e.,

$$\boldsymbol{q} = u_r \boldsymbol{i}_r + u_z \boldsymbol{i}_z \tag{3.1}$$

or in terms of the Stokes' stream function

$$\boldsymbol{q} = \left(\frac{1}{r}\frac{\partial \psi}{\partial z}\right)\boldsymbol{i}_r + \left(-\frac{1}{r}\frac{\partial \psi}{\partial r}\right)\boldsymbol{i}_z \tag{3.2}$$

and the vorticity is given by

$$\omega = \frac{1}{r}\mathrm{E}^2\psi. \tag{3.3}$$

In this case the equations of motion are given by (1.1 *a*), (1.2 *a*) and (1.3 *a*) with $\chi = 0$.

The condition of integrability (1.8) becomes

$$\begin{aligned} r\mathrm{J}\begin{pmatrix}\psi & r^{-2}\mathrm{E}^2\psi\\ z & r\end{pmatrix} &= \nu\mathrm{E}^4\psi + 2\nu_c\left\{\frac{2}{r}\mathrm{J}\begin{pmatrix}\psi & r^{-2}\mathrm{E}^2\psi\\ z & r\end{pmatrix} - 2\mathrm{J}\begin{pmatrix}\frac{\partial\psi}{\partial r} & r^{-2}\mathrm{E}^2\psi\\ z & r\end{pmatrix}\right.\\ &\left. - \frac{1}{r^2}\frac{\partial\psi}{\partial z}\mathrm{E}^4\psi - \frac{\partial}{\partial z}\left(\frac{1}{r}\mathrm{E}^2\psi\right)^2 + \frac{2}{r}\frac{\partial\psi}{\partial z}\frac{\partial}{\partial r}\left(\frac{\mathrm{E}^2\psi}{r^2}\right)\right\} \end{aligned} \tag{3.4}$$

while the condition (1.9) is automatically satisfied.

The condition of superposability (1.10) for two axi-symmetrical flows with stream functions ψ_1 and ψ_2 is given by,

$$\begin{aligned} &\mathrm{J}\begin{pmatrix}\psi_1 & r^{-2}\mathrm{E}^2\psi_2\\ z & r\end{pmatrix} + \mathrm{J}\begin{pmatrix}\psi_2 & r^{-2}\mathrm{E}^2\psi_1\\ z & r\end{pmatrix}\\ &= \frac{2\nu_c}{r}\left\{\frac{2}{r}\mathrm{J}\begin{pmatrix}\psi_1 & r^{-2}\mathrm{E}^2\psi_2\\ z & r\end{pmatrix} + \frac{2}{r}\mathrm{J}\begin{pmatrix}\psi_2 & r^{-2}\mathrm{E}^2\psi_1\\ z & r\end{pmatrix}\right.\\ &\left. - 2\mathrm{J}\begin{pmatrix}\frac{\partial\psi_1}{\partial r} & r^{-2}\mathrm{E}^2\psi_2\\ z & r\end{pmatrix} - 2\mathrm{J}\begin{pmatrix}\frac{\partial\psi_2}{\partial r} & r^{-2}\mathrm{E}^2\psi_1\\ z & r\end{pmatrix}\right. \end{aligned}$$

$$- \frac{1}{r^2}\frac{\partial \psi_1}{\partial z} E^4\psi_2 - \frac{1}{r^2}\frac{\partial \psi_2}{\partial z} E^4\psi_1 + \frac{2}{r}\frac{\partial \psi_1}{\partial z}\frac{\partial}{\partial r}\left(\frac{E^4\psi_2}{r^2}\right)$$

$$+ \frac{2}{r}\frac{\partial \psi_2}{\partial z}\frac{\partial}{\partial r}\left(\frac{E^4\psi_1}{r^2}\right)\Bigg\}. \tag{3.5}$$

The condition (1.11) is automatically satisfied. The condition for self-superposability of this flow is given by:

$$J\begin{pmatrix}\psi & r^{-2}E^2\psi\\ z & r\end{pmatrix}$$

$$= \frac{2\nu_c}{r}\left\{\frac{2}{r}J\begin{pmatrix}\psi & r^{-2}E^2\psi\\ z & r\end{pmatrix} - 2J\begin{pmatrix}\frac{\partial\psi}{\partial r} & r^{-2}E^2\psi\\ z & r\end{pmatrix}\right.$$

$$\left. - \frac{1}{r^2}\left(\frac{\partial\psi}{\partial z}E^4\psi + \frac{2}{r}\frac{\partial\psi}{\partial z}\frac{\partial}{\partial r}\left(\frac{E^2\psi}{r^2}\right)\right)\right\}. \tag{3.6}$$

From the condition (3.5), we see that a rotational flow with suffix 2, is superposable on an irrotational flow with suffix 1, if

$$J\begin{pmatrix}\psi_1 & r^{-2}E^2\psi_2\\ z & r\end{pmatrix}$$

$$= \frac{2\nu_c}{r}\left\{\frac{2}{r}J\begin{pmatrix}\psi_1 & r^{-2}E^2\psi_2\\ z & r\end{pmatrix} - 2J\begin{pmatrix}\frac{\partial\psi_1}{\partial r} & r^{-2}E^2\psi_2\\ z & r\end{pmatrix}\right.$$

$$\left. - \frac{1}{r^2}\frac{\partial\psi_1}{\partial z}E^4\psi_2 + \frac{2}{r}\frac{\partial\psi_1}{\partial z}\frac{\partial}{\partial r}\left(\frac{E^2\psi_2}{r^2}\right)\right\}. \tag{3.7}$$

Using the conditions (3.5) and (3.6), we can prove the following theorems.

THEOREM 1.—*All irrotational motions are self-superposable and any two irrotational motions are superposable on each other.*

THEOREM 2.—*The two flows will be superposable if the vorticity of each flow is proportional to* r. *Also an axi-symmetrical flow will be self-superposable if its vorticity is proportional to* r.

THEOREM 3.—*If* ω_1/r *is constant along the stream lines of flow* 2, *while* ω_2/r *is constant along the stream lines of flow* 1, *then the two flows are superposable if in addition the velocity components and vorticities satisfy the condition*

$$2(u_1v_1 + u_2v_2) + r(v_1\omega_1 + v_2\omega_2) = 0.$$

(*where* ω_1 *and* ω_2 *are the vorticities of the two flows*).

THEOREM 4.—*An axi-symmetrical flow is self-superposable, if the vorticity* ω *is of the form* $\omega = f(\psi)\, r$ *and if the stream function* ψ *satisfies the condition*

$$E^4\psi = 2r \frac{\partial}{\partial r}\left(\frac{1}{r^2} E^2\psi\right).$$

While the condition of integrability reduces to

$$\nu E^4\psi = \frac{2\nu_c}{r^2} \frac{\partial}{\partial z}(E^4\psi).$$

Also a rotational flow with stream function ψ_2 is superposable on an irrotational flow with stream function ψ_1, if in general

$$\omega_2 = f(\psi_1)\, r$$

and

$$E^4\psi_2 = 2r \frac{\partial}{\partial r}\left(\frac{1}{r^2} E^2\psi_2\right).$$

The corresponding theorems for a Newtonian fluid have been given by Bhatnagar and Verma.[3]

I am deeply grateful to Prof. P. L. Bhatnagar for suggesting the problem and for his kind guidance throughout this work.

REFERENCES

1. Braun and Reiner, M. .. *Quar. Jour. Mech. and App. Math.*, 1952, **5**, 42–53.
2. Lakshmana Rao, S. K. .. *Proc. Ind. Acad. Sci.*, 1957, **45 A**, 418–23.
3. Bhatnagar, P. L. and Verma, P. D. *Ibid.*, 1957, **45 A**, 281–92.

KINETICS OF THE OLEFINE BROMINE REACTION

Part 12. Addition to Allyl Compounds

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Introduction

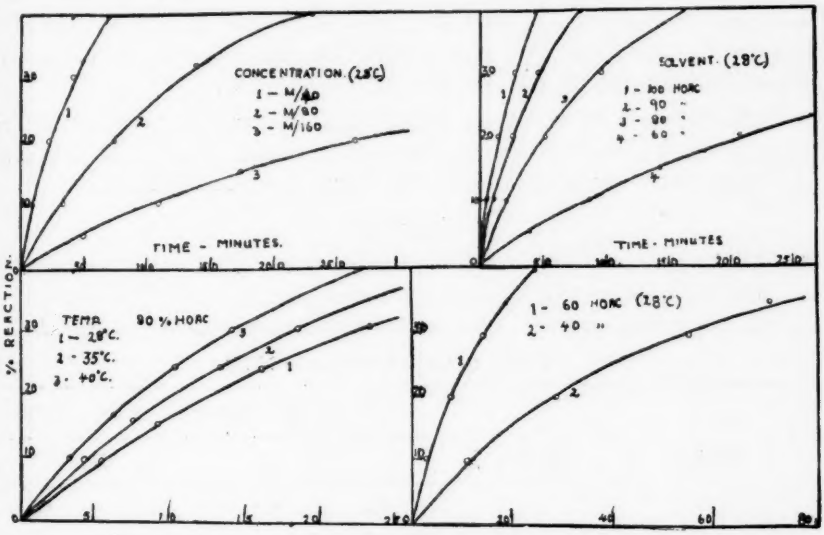
The kinetics of bromine addition to α-β unsaturated acids under various conditions have been reported from time to time.[10] The reaction in acetic acid is homogeneous, while in the non-polar solvent carbon tetrachloride is heterogeneous.[2] A termolecular addition with increasing 'bimolecular rate constants' has been reported for allyl chloride and allyl bromide by Robertson *et al.*[14a] in acetic acid below 30° C. and the influence of electrolytes on the addition reaction has also been studied. Nozaki and Ogg[13] studied the reaction in acetic acid, while Juvala[8] used carbon tetrachloride where the normal electrophilic addition (allyl bromide faster than allyl chloride) has been reported. But Robertson *et al.* were unable to confirm Juvala's observation even in an atmosphere of dry nitrogen. It was expected that a study of the thermal addition of bromine to allyl compounds—allyl chloride, allyl bromide, 2-methyl allyl chloride and allyl propionate—in acetic acid and in acetic acid-carbon tetrachloride solvent mixtures at different temperatures would lead to a better understanding of both structural and solvent influences.

Experimental

Materials Used.—Bromine, acetic acid and carbon tetrachloride were purified as in earlier communications.[10] Allyl chloride and allyl bromide were purified by the method of Vogel.[15] Calcium bromide was used for drying allyl bromide, while 2-methyl allyl chloride was purified by the same method as allyl chloride. Allyl propionate was washed with a saturated solution of sodium bicarbonate and then with water, and dried over a prolonged period by calcium chloride and fractionated. Periodic purification before use was found to be necessary with all allyl halides. The compounds were stored in amber-coloured bottles in the dark, in desiccators over fused anhydrous calcium chloride.

Allyl chloride	..	45° C. (758 mm.).
Allyl bromide	..	70° C. (759 mm.)
Allyl propionate	..	123° C. (760 mm.)
2-methyl allyl chloride	..	72·2° C. (757 mm.)
Acetic acid	..	118° C. (760 mm.) $[n]_D^{30} = 1·3672$
Carbon tetrachloride	..	76·8° C. (760 mm.) $[n]_D^{30} = 1·4539$

Solvent mixtures were prepared by adding together appropriate volumes of each component, taking the usual precautions. These mixtures were used for preparing the standard solutions of olefine and bromine. All weighings were carried out only in weak diffused light, due to the sensitivity of allyl compounds to light. Typical experimental results are presented in Figs. 1, 2, 3 and 4.



FIGS. 1–4. Fig. 1. Allyl Bromide. 80% HOAc. Fig. 2. Allyl Chloride (M/80). Fig. 3. Allyl Propionate (M/160). Fig. 4. 2-Methyl Allyl Chloride (M/80).

In all cases, the reaction is homogeneous, differing from the olefine-acids, which in pure carbon tetrachloride were found to show heterogeneous addition. Since Robertson *et al.* [16b] had reported a termolecular addtion, the termolecular rate constants were calculated by the equation

$$K_3 = \frac{2}{t}\left\{\frac{1}{(a-x)^2} - \frac{1}{a^2}\right\}.$$

DISCUSSION OF RESULTS

Robertson has reported that the order of the reaction between allyl chloride and bromine, at concentration 0·04 to 0·02 M, was 3·2, somewhat higher than the values 3·0 to 3·1 obtained for other compounds over this concentration range, and this higher value has been attributed possibly to autocatalysis. He considered that Nozaki and Ogg's data show an order 3·3 and 3·7. The present results too appear to indicate a third order, the order with respect to olefine being invariably one. The increasing bimolecular constants obtained by them with the progress of the reaction clearly indicated autocatalysis. Retardation by the dibromides may not be pronounced in acetic acid, as is shown by our investigation. The hydrogen bromide formed acts as a catalyst in the case of olefine acids, but the effect may not be as pronounced for allyl compounds as for acids, since substituents may be less deactivating in the former group of compounds. An order greater than two is consistent with decreasing K_2 values, while increasing K_3 values may indicate an order less than three in the absence of disturbing influence on the reaction, as autocatalysis.

We find that in all cases, bimolecular constants decreased with the progress of the reaction up to about 40% completion of the reaction but fairly good termolecular constants have been obtained.

TABLE I

Bimolecular constants (K_2) and termolecular constants (K_3) for the reaction between bromine and allyl chloride, and bromine and allyl bromide in the solvent mixtures (Acetic acid-Carbon tetrachloride) at 28° C.

(Concentration of reactants = M/80)

Olefine	Solvent %	Value for % completion of the reaction			
		K_2		K_3	
		10	40	10	40
Allyl chloride ..	100 HOAc	1·347	1·088	454·9	453·4
..	90 „	0·8081	0·6311	273·0	269·3
..	80 „	0·4136	0·3194	139·7	136·3
..	60 „	0·1022	0·0833	34·51	35·56
Allyl bromide ..	100 „	1·1117	0·9155	395·1	390·4
..	90 „	0·5926	0·4618	200·2	192·5
..	80 „	0·2778	0·2265	93·83	96·63
..	60 „	0·0773	0·0591	25·66	25·23

In all cases K_2 values are presented as moles per litre per minute and K_3 values as (moles per litre)$^{-2}$ per minute.

The tendency for the termolecular constants to increase is also noted in the later stages of the reaction at lower concentration of allyl propionate and 2 methyl allyl chloride. This can be ascribed to catalysis by hydrogen bromide formed during the course of the reaction and also the gradual dominance of the bimolecular reaction over the termolecular one. Further, it is seen that the termolecular constants appear to show an inverse variation with concentration, indicating clearly a composite mechanism of bimolecular and termolecular types. The bimolecular reaction may not be so pronounced during the initial stages at the concentration investigated.

TABLE II

Effect of concentration changes on K_3 values ($K_3 \times 10^{-2}$)

(Solvent: Acetic acid-Carbon tetrachloride mixture. Temperature 28° C.)

Olefine	Solvent %	Concentration		
		M/80	M/160	M/320
2-methyl allyl chloride	100 HOAc	..	..	218·30*
„	80 „	..	43·32	48·04*
„	60 „	9·871	10·87	12·49
„	40 „	2·45	2·425	2·734
Allyl propionate ..	80 „	17·29	23·04	..
„ ..	60 „	7·285	8·668	..
„ ..	40 „	2·205	2·779	..

* At 10% completion of the reaction.

The reaction shows a pronounced sensitivity to added water (Fig. 5). In 99% acetic acid (1% water) K_2 increases initially and with increased amounts of water K_2 tends to remain constant, whereas in pure acetic acid, K_2 decreases. This may be the resultant of two changes: a change in the polarity of the environment and formation of the hydrogen bromide by interaction of water with bromine. The termolecular reaction thus becomes a bimolecular one and the increasing K_2 values arise from autocatalysis.

An analysis of earlier work clearly indicates that in the addition of bromine, increased dilution of reactants, rise of temperature, or small increase in water content of the solvent results in a gradual dominance of a second order rate with a higher heat of activation. The tendency of K_3 values to increase with the progress of the reaction is greater in the more dilute solutions and also at the higher temperature. We find the same trend.

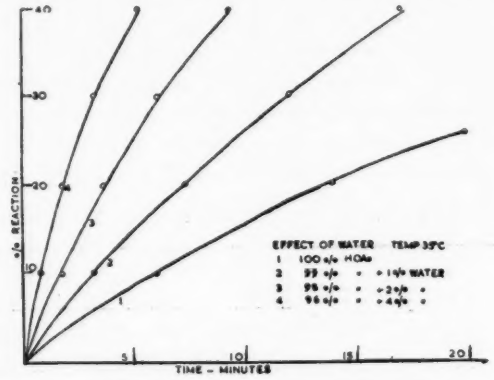


FIG. 5. Allyl Chloride (M/80).

The change of order with dilution may now be analysed. When the halogens and the olefines react, the first result is the apparent formation of a 1 : 1 molecular complex.[4] The termolecular process may then be written thus:

$$A + Br_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} [A, Br_2] \xrightarrow[K_3]{Br_2} ABr\cdot Br\cdot + Br_2 \qquad \left\{\begin{array}{l} A = \text{Olefine.} \\ C = \text{Catalyst, solvent (hydroxylic) or bromine.} \end{array}\right.$$

$$\xrightarrow[K_3]{C} ABr\cdot Br + C$$

The rate of formation of the complex (A, Br_2) will be proportional to the encounters between olefine and bromine, and the rate of disappearance will be the sum of two factors: the decomposition of (A, Br_2) into A and Br_2 and their disappearance in the actual chemical transformation.

$$\frac{d\,[ABr_2]}{dt} = K_1\,(A)\,(Br_2) - K_2\,[A, Br_2] - K_3\,[ABr_2]\,[C]$$

Since for the steady state $d\,[A, Br_2]/dt = 0$, the rate of reaction is equal to

$$K_3\,[ABr_2]\,[C] = \frac{K_3 \cdot K_1 \cdot (A)\,(Br_2)\,(C)}{K_2 + K_3\,(C)}.$$

At low concentrations of bromine ($C = Br_2$), the reaction rate is thus proportional to $(A)(Br_2)^2$ and at high concentration, the rate is proportional to $(A)(Br_2)$.

According to Robertson in the concentration region $(M/20) - (M/80)$ in acetic acid, the reaction is termolecular. Even at lower concentration in acetic acid, carbon tetrachloride solvent mixtures, the reaction appears to be termolecular. The rate thus appears to be proportional to $(A)(Br_2)^2$. The decrease in order with dilution in acetic acid and the apparent bimolecular constants as well as the observed bimolecular reaction in solvents more polar than acetic acid has then to be accounted for. With increasing dilution the place of a second bromine molecule is apparently taken by the acetic acid molecules and in the more polar solvents this is even more so. Hence, the reaction

$$[ABr_2] \rightarrow ABr^+ + Br^-$$
$$\downarrow HOAc$$
$$ABrOAc + H^+$$
$$ABr^+ + Br^- \rightarrow ABrBr.$$

The primary association of olefine and bromine thus becomes the rate determining step. The bromine addition in methyl alcohol is bimolecular[3] because of the higher dielectric constant which facilitates polarisation of the bromine molecule and the greater reactivity of $(OMe)^-$ compared to the $(OAc)^-$. Catalysis by HBr may not be so pronounced for a termolecular reaction. It has been observed by Nozaki and Ogg that more bromide ions are formed at lower concentration of bromine in acetic acid during the reaction. According to Andrews[9] in aromatic halogenation in hydroxylic solvents, the place of bromine is replaced by the solvent. Hence in the equation:

$$-\frac{dBr_2}{dt} = K_2(A)(Br_2) + K_3(A)(Br_2)^2$$

K_2 and K_3 correspond to the functioning of acetic acid and bromine as electrophilic reagent in promoting the anionisation of Br_2 from the complex (A, Br_2).

Effect of temperature, substituents and solvents can be assessed from Tables III and IV. It can be seen from Table III that a plot of log K against $1/T$ will not be a straight line indicating a mechanistic change with temperature; the energy of activation increases with temperature.

TABLE III

Effect of temperature : 2-methyl allyl chloride and bromine reaction
Concentration of reactants: M/160

(Solvent: Acetic acid-Carbon tetrachloride mixture)

Solvent %	Temperature	K_3	E K.cal.	Average E	PZ
80 HOAc ..	28	4332			
	35	4642	1·82 / 3·34	2·58	$5·1\times10^8$
	40	5041			
60 HOAc ..	28	1081			
	35	1145	1·37 / 2·37	1·87	$4·0\times10^8$
	40	1218			
40 HOAc ..	28	242·5			
	35	247·0	0·49 / 1·17	0·83	$3·0\times10$
	40	254·2			

TABLE IV

Effect of substituents

(Solvent: 60% HOAc, 40% CCl_4)

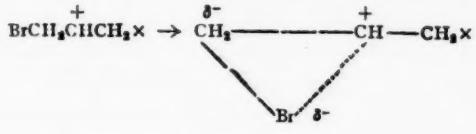
	Allyl chloride	Allyl bromide	2-methyl allyl chloride	Allyl propionate
	M/80	M/80	M/160	M/160
E. K. Cal. (Average) ..	1·08	3·82	1·87	4·69
$\log_{10}$PZ ..	0·55	2·38	2·60	4·54

Changes in the Arrehenius parameters follow the same trend except for allyl bromide, where there seems to be a decrease in the apparent order of the reaction with increase in carbon tetrachloride content of the medium.

The values of the frequency factor decrease in all cases with more of carbon tetrachloride but the decrease is not so great for allyl bromide. The change in the value of E and PZ can arise from an increase participation of a termolecular mechanism, with increasing carbon tetrachloride content which in its turn decreases the apparent polarity of the solvent. A study of absorption spectra[11] of bromine in acetic acid and carbon tetrachloride indicates clearly the solvation effects in hydroxylic solvents. The acetic acid may be forming a semi-rigid cage around the bromine molecule with the resultant electrostatic polarisation of the halogen molecule. The extent of this decreases with the decreasing polarity of the solvent. This view is supported by the linear plots obtained for log K_3 against (D−1)/(2D+1) for this dipole reaction (Fig. 6).

Using the conventional rate equation, we have $K_3 = PZ_3e^{-E/RT}$ where Z_3 is the collision rate at unit concentration. For a termolecular reaction Z_3 is of the order 10^9 to 10^{12}, 1^2 moles^{-2} sec.$^{-1}$ and the values of P is of the order 10^{-5} to 10^{-10} in reaction involving polyatomic molecules,[6,7] low values of the frequency factor have to be expected and the results bear this out.

Migration of groups as well as the relative stability of carbonium ion which in its turn is affected by the presence of substituents cannot be excluded in the addition of electrophilic reagent such as HOCl to the allyl halides.[5] Now the bromine addition to allyl halide may be pictured thus:



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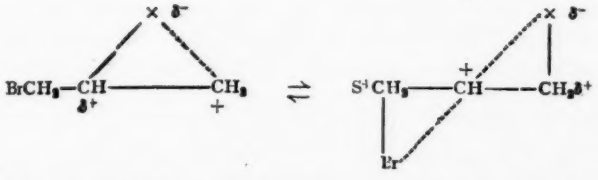


When X = Br, the possibility of the chances of such a structure will be increased when compared with allyl chloride, *i.e.*, such complete equivalence may not be expected for allyl chloride as for allyl bromide for the bromine addition reaction. This can account for the difference between allyl chloride and allyl bromide, in the latter compound the decrease in the frequency

factor is less. Two products of bromine addition to allyl chloride are possible, namely, $CH_2BrCHBrCH_2Cl$ and $CH_2BrCHClCH_2Br$ while for allyl bromide the sole product of the bromine addition is $CH_2BrCHBrCH_2Br$ assuming only the dibromide formation. This aspect can only be confirmed with tracer techniques. Further, the halogen hyperconjugation will be greater for allyl chloride than in allyl bromide. Electron releasing groups in the 2-position should stabilise the carbonium ion and allow it to last for a longer life before reaction with the nucleophilic part. In this way, the reaction through the symmetrical intermediate may be favoured for 2-methyl allyl chloride and as a result the products may be $CH_2BrC(CH_3)ClCH_2Br$ and $CH_2BrC(CH_3)BrCH_2Cl$. Complete equivalence of the halogen may not be expected since chlorine is more electronegative than bromine and the products formed will not be in equal proportions. This is considered in a later communication.

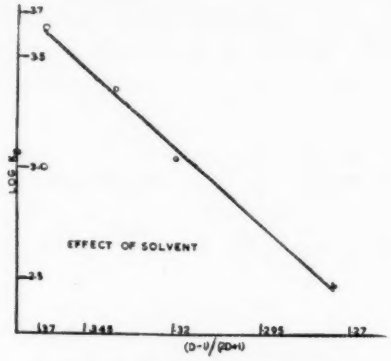


FIG. 6. Allyl Bromide (M/160).

In the series, 2-methyl allyl chloride, allyl propionate, allyl chloride and allyl bromide, in pure acetic acid, the reactivity decreases in the order, but the addition of carbon tetrachloride brings about a change, allyl propionate becoming faster than 2-methyl allyl chloride, as is seen from Table V.

The relative reactivity of allyl chloride and bromide has been attributed by Robertson *et al.* to the two modes of reaction: (1) due to hydrogen hyperconjugation and (2) due to the inductive effect of the halomethyl group. This may be extended, in the present case, to 2-methyl allyl chloride. The methyl group facilitates the initiation of the addition at the ethenoid carbon atom remote from the methyl group (Carbon $-$ 1) $+$ I effect of methyl group thus augments the C—H hyperconjugation of the methyl group as well as that of the chloromethyl group which in its turn is effected

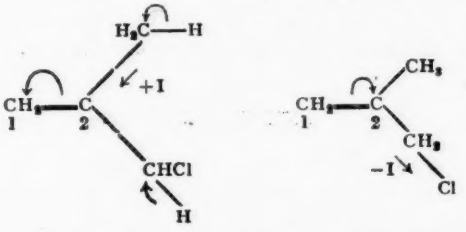
TABLE V

Influence of substituents and solvent composition (concentration M/160)

(Solvent: Acetic acid-Carbon tetrachloride mixture)

Solvent %		Allyl chloride	Allyl bromide	2-methyl allyl chloride	Allyl propionate
80 HOAc	..	149·5	110·1	4332	2304
60 „	..	38·58	30·05	1087	866·8
40 „	..	..	..	242·5	277·9

by −I effect of the chlorine, and the −I effect can initiate the addition at carbon −2 as shown below.



Further, the polarising forces of the methyl and chloro-methyl groups are −0·39 and +0·36 C.G.S. units[13] and this indicates that initiation of addition at carbon (1) is more important.

The rate of addition of bromine to propylene is greater than allyl chloride by a factor greater than 10^3. By reference to the reactivities of ethylene and allyl chloride, the reactivity of bischloro-ethylene is given as 1 : 0·019 : 0·00024. 2-methyl allyl chloride is found to be faster than allyl chloride by a factor of 30. Hence, 2-methyl allyl chloride adds bromine considerably rapidly when compared with bischloro-ethylene, the rate factor being greater than 10^3, as must be expected due to the powerful electron withdrawing influence of the halogen substituent. Hence the slow addition of bischloro-methyl ethylene cannot be attributed to steric hindrance, even if it operates, it will be of minor importance.

In allyl propionate −I effect of 'CO' may not have an appreciable effect on the ethylenic system for it is far removed from the ethenoid centre. Hence, allyl propionate must be faster than allyl halides. Further, it gives

a clear evidence for a composite mechanism—both bimolecular and termolecular—are operative and the bimolecular reaction slowly changes over to a termolecular one with a decrease in the polarity of the solvents. This, in turn, is reflected in the energy of activation and frequency factor. Unlike $\alpha-\beta$ unsaturated acids, addition to allyl compounds does not indicate any high degree of autocatalysis.

Hence, it is clear that in comparing the influence of substituents, the velocity constant alone is inadequate. Further, if one compares the reactivity using the velocity constant, there is the implicit assumption that frequency factor is identical for all the olefines and this assumption can, by no means, be justified. Substituents may not influence equally in the gas phase and in solution and may also vary with the solvent (*cf.* 1).

SUMMARY

The thermal addition of bromine to allyl compounds has been studied in acetic acid–carbon tetrachloride solvent mixtures at various temperatures. The influence of solvents and substituents on the reaction mechanism has been discussed.

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REFERENCES

Anantakrishnan, S. V. .. *Proc. Ind. Acad. Sci.*, 1948, **27 A**, 184.

2. ——— and Mathai, I. M. *Curr. Sci.*, **1954**, **23**, 219.
3. Bartlett and Tarbell .. *J. Amer. Chem. Soc.*, 1936, **58**, 466.
4. Buckles, R. E. and Yuk .. *Ibid.*, 1953, **75**, 5048.
5. de-la Mare, P. B. D. and Pritchard *J. Chem. Soc.*, 1954, 3990.
6. Frost and Pearson .. *Kinetics and Mechanism*, John Wiley, 1953, 72.
7. Glasstone, Laidler and Eyring *Theory of Rate Process*, McGraw-Hill Book Co., 1949, 19.
8. Juvala .. *Ber.*, 1930, **63**, 1998.
9. Keefer, R. M. and Andrews *J. Amer. Chem. Soc.*, 1957, **79**, 4348.
10. Mathai, I. M. .. *J. Sci. Industr. Res.*, 1958, **17 B**, 149.
11. *Supplement to Mellor's Comprehensive Inorganic and Theoretical Chemistry*, Supplement 2, Part I, Longmans, pp. 784.

12. Nazoki, K. and Ogg, R. A. (Jr.) *J. Amer. Chem. Soc.*, 1942, **64**, 709.

13. Price, C. C. .. "Reactions at Carbon-Carbon double bonds," *Inst. Sci. Pub.*, 1946, 27.

14. (*a*) Robertson, P. W. *et al. J. Chem. Soc.*, 1952, 1014.
(*b*) ———— .. *Ibid.*, 1937, 335.

15. Vogel, A. I. and Jeffery .. *Ibid.*, 1948, 666.

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CONTENTS

PAGE

Design and Operation of a Molecular Oscillator . . . . . H. G. Venkates and M. W. P. Strandberg 123

On the Application of the Matrix Calculus in the Theory of Geometrical Difference Equations . . . . . W. Hahn 137

Intensity Studies in Raman Effect: Effect of Conjugation . . . . . K. Venkateswarlu and K. Ramaswamy 146

Intensity of Raman Lines in Carboxylic Acids, Esters and Nitriles . . . . . K. Venkateswarlu and C. Balasubramanian 151

Superposability of Steady Axi-Symmetrical Flows in a Non-Newtonian Fluid . . . . . (Miss) S. L. Rathna 155

Kinetics of the Olefine Bromine Reaction. Part 12. Addition to Allyl Compounds . . . . . I. M. Mathai 164